STUDIES ON THE METALLIC POLLUTION IN SOIL

A

Thesis Submitted for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF ALLAHABAD

By

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M.Sc. (Gold Medalist)

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UNIVERSITY OF ALLAHABAD

ALLAHABAD

November 2002

I. C. No.: SD13/0016 Enrollment No.: 96-AU-109

Dedicated

to My

Venerable Parent

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CERTIFICATE

*This is to certify that **Sri Abhaya Pratap Singh** has conducted research work under my supervision on the topic entitled **"Studies on the Metallic Pollution in Soil"** for the award of the degree of Doctor of Philosophy in Agriculture and Soil Science of the Allahabad University. To the best of my knowledge the data presented in the thesis are genuine and original.*

Dinesh Mani
(DINESH MANI)

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Acknowledgement

I am highly indebted to my guide **Dr. Dinesh Mani**, Senior Lecturer, Sheila Dhar Institute of Soil Science, University of Allahabad for taking his keen interest, valuable suggestions, constructive criticism and everlasting zeal which he showed in solving several intricate problems during the course of present study and successful completion of this manuscript to its final form. It would have never been possible for me to complete the work and prepare the thesis without his sympathetic and helpful attitude.

I am also thankful to **Prof. Bharat Singh**, Head, Chemistry Department and **Prof. M.M. Verma**, Ex. Head, Chemistry Department and Ex-Director Sheila Dhar Institute of Soil Science for their valuable suggestions and help during the entire course of my study at this institute.

I am grateful to **Dr. Arvind Singh** and all my friends and well wishers specially, Jai Prakash Singh, Chitranjan, Dhritanjai, Ved Prakash, Ajay Kumar, Prabhat, Shailendra Vikram, Pankaj Kumar, Divya Pratap who helped me during the entire course of my research work.

I am highly indebted to my venerable father **Shri S.B. Singh** and mother **Smt. Pushpa Singh**, brother **Mr. N.P. Singh** and **Mr. A.K. Singh** and other family members for their kind help, affection, inspiration, co-operation and moral support throughout my study period to reach this destiny cheerfully.

A grateful acknowledgement is also due to the University of Allahabad, for providing me N.R. Dhar Memorial Scholarship during the period of research work.

Last but not least, I also thank to all the staff members of this Institute who helped me from time to time.

Lastly, I also thank to Mr. Ajay and Dhiraj (Aparna Computer Point, Katra, Alld.) for typing this manuscript.

Allahabad,
November, 2002

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Contents

LIST OF TABLES

Chapter I

INTRODUCTION

Chapter – I

INTRODUCTION

The chemical aspects of environmental pollution and their remedial measures mostly in reference to the build up of the concentration of toxic metals and compounds in the environment are burning issues to be discussed today. The environmental effect of chemical compounds can be considered to be a disturbance in the ecosystem in terms of an increase in the concentration of metal ions and organic compounds beyond their natural levels in plant and animal life as well as in air, water, soil and sediments.

Considering the bio–inorganic aspect of pollution, metal ions can be classified into essential and toxic based on their biological requirement. Even an essential element like copper requirement in trace quantities for various metabolic processes can become toxic in concentration exceeding the biological limits. The toxic elements like Hg, Cd, Pb, Pd, Pt, Sn, Sb, As and Ge find their way through complexing with suitable organic molecules into the geosphere, to fresh and marine water and to plants and animals.

The three interacting entities–plant, soil, and sludge– may be considered in order. First, different species of plants differ greatly in their uptake of each metal, and not only do species differ but so do varieties, so that one might find a tolerant strain of a generally sensitive species. Most of the common grasses and grain crops are tolerant of these heavy metals, while the leafy vegetables, especially the beets, are easily damaged.

Second, soils differ in two ways, first in colloid content (which we

may define as material less than one–fifth a micrometer in diameter, 0.0002 millimeter) and second in pH. The full mechanism by which they bind heavy metals is not well known and is controversial, but at least this is agreed. The organic colloid ("humus") may be five times as effective as the same percentage of clay (the inorganic colloid). But the effect depends on pH, with a sharp increase in binding from 6 upwards. Thus acidic soils involve far more risk of damage than do those close to neutrality.

Third, sludge itself inactivates the heavy metals which it incorporates, in two ways. First, by virtue of its own organic composition; second, by its content of inorganic phosphorus, namely 2 or 3 percent of dry weight, to quote a common value in the United States. This phosphate antagonizes the heavy metals inside the plant, rather than within the soil.

Information on the heavy application of heavy metals with sewage wastes may come from continuous usage over many years or from a single application at a heavy rate. The question of whether these two treatments give similar or contrasting results leads us into the controversy just referred to– namely, what is the binding mechanism?

In short, soil is a universal precipitating agent by virtue of its colloidal constituents. The form into which a heavy metal is immediately bound may be loose enough to allow a substantial proportion to move a little and to enter and damage plants. But in the days or months after its addition to soil it is likely to rearrange into ever more stable and less soluble forms. While some exact statements may be made about the ultimate, most stable and least soluble forms, such statements do not help us; our problem is at what rate the rearranging happens, and here no answer

is given by theory, and conflicting answers may be given in practice. It has long been known that light applications of zinc (2 or 3 pounds/acre) disappear from circulation within a few days, but this is not true of 200 or 300 pounds/acre. When zinc has been added to soil with sludge, two opposing effects follow in the next few years: on the one hand, the organic components of the sludge, which had been helping to bind it, are destroyed by microbial oxidation on the other, its compounds with other components of the soil are rearranging themselves towards lower solubility. One of the debatable issues in this complex affair is how much credit to give to the soil for its protection and how much to sludge. The sludge may be very efficient while it lasts, but it may oxidize away so that half has disappeared in 3 or 4 years– that is, its protecting power is halved. In general, zinc and cadmium remain more soluble for longer in soils than do copper and nickel, so call for more serious attention when sludge is added.

In all such experiences, whether practical as in city sewage farms, or partly or wholly experimental, the major cases of direct damage by heavy metals added in sewage or sludge have been with vegetable crops, whether by zinc, copper, or nickel. Indirect damage by the antagonism of zinc against manganese or (probably against has been noted, but such antagonisms are easily dealt with in the field.

Sewage or sludge may be applied to land simply as a way of disposing of a nuisance. Thought of in this way, one may favorably compare the addition of the accompanying heavy metal to a soil, from which it does not move further, with the two alternative disposals, namely to the air (by incineration) or to water, both of which increase the general

environmental level of a noxious metal. But application to the land does much more than dispose of a nuisance, since it simultaneously allows some of the major nutrients to be recovered, and while initially it may be thought of as providing revenue for a municipal farm, it can confer agricultural benefit on a wider scale. One aim may be to use up the organic nitrogen and so to recycle the nitrogen in growing crops. In such a case the total amounts applied are themselves heavy. But in all such cases the amount of phosphorus applied is enormous, being many times as much as would be needed for the maximum yield of a crop. From this line of thought comes the proposal to recycle, not nitrogen but phosphorus, so to limit the application of sewage sludge to the amount of phosphate required for one cropping year. This involves reducing the addition of heavy metal to about one–fiftieth or one–hundredth of the amount previously discussed– or otherwise expressed, spreading it over fifty or one hundred times the area. This greatly postpones any future day of reckoning. The heavy metals will still accumulate in the surface soil, but only zinc and cadmium are likely to remain active enough in soil over the decades to enter into food chains, and of these only cadmium is a serious hazard. Now that its noxiousness is recognized one may expect that its addition to sludges will be steadily reduced; and more will be learned about the crops and varieties that exclude it from their edible parts.

The heavy metals added with the sludge may be in one of many forms of combination including oxide, sulfide, phosphate, or adsorbed by the sludge colloids. After the sludge has been incorporated the new system– whether 10 or 50 parts of soil to 1 of sludge – will gradually reorganize

itself. From time to time some of the metal ions will appear in solution; an oxide may be converted into soluble bicarbonate, or a sulphide may be converted microbially to sulphate. While many ions will long remain attached to colloidal particles of sludge, we may first consider the alternatives in front of any ion entering the solution. It may either (1) stay in solution and pass out eventually into drainage, (2) be taken up by a plant growing on the soil, which may later be harvested and removed, (3) disappear in the gaseous phase, or (4) be held by the soil in a temporarily or permanently insoluble form.

Some of these added metals are in a form, or are converted into a form, in which they remain immobile, neither entering into solution nor into a biological cycle. This is clearly so with chromium, which form the insoluble oxide Cr_2O_3. Lead and mercury added to soil have likewise shown no trace of increasing in plant uptake or of entering into drainage. The statement that mercury rates no more than this mention may surprise a reader who knows of the harm done to aquatic life by discharges of mercury into lakes and estuaries. But these are quite different situations from soil. In water, mercury may be carried on very fine suspended particles and may even be dissolved off these particles on meeting the salt sea. But applied in sludges to soil, it is strongly precipitated on the spot so is filtered out, and is not taken up at all by roots, so that unlike its toxic relative cadmium it does not enter the food chain. Lead too may endanger life through aerial contamination, but not by entering the edible parts of plants by way of the soil. Tin (of which less is known in soil chemistry than of lead) similarly shows no evidence of entering into circulation. So these

four may be regarded as no different from titanium in their performance in soils.

Molybdenum has been included in this first full list, but it does not call for more than a passing mention. A few soils are known in which molybdenum enters pasture plants in amounts toxic for livestock, but none are known in which molybdenum from sewage wastes has led to any such toxicity, and the amounts so added are likely to remain too small for concern. There remain zinc, copper, nickel and cadmium, all of which must be considered individually: zinc, copper, and nickel, because all are on record as having damaged certain crops when applied with sewage sludge; and cadmium, because it is on record as having accumulated in some plants to levels dangerous to the consumer.

Sludge contains a large number of polluting elements mainly originating from industrial activity. They are often present in larger amounts in sludge than in soil or plants. Elements like copper (Cu), manganese (Mn), Selenium (Se) and zinc (Zn) are essential (necessary) to plants and animals, but other elements like nickel (Ni), chromium (Cr) arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) have no special function in plants and animals and applied to soil used for production of fodder or food they are to be considered as unwanted and toxic.

Application of larger amounts of heavy metals to the soil can cause an accumulation, and continued accumulation of large amounts might lead to potential toxicity. Leaching of heavy metals to ground water is very low due to their very low solubility. The most serious factor connected to heavy metals in sludge and its use in agriculture is the risk of accumulation and

concentration through the food–chain with risk of intoxicating man and animal. In this connection the type of soil, pH and type of crop play a very significant role. Soil with a good cation exchange capacity in connection with clay or humus content are able to absorb larger amounts of heavy metals, why application to such soils results in a relatively lower plant availability.

Humus and other organic compounds can chelate with metals and create stable complex compounds whereby the availability towards plants can be reduced. The organic colloid of soil has a far greater c.e.c., weight for weight, than the inorganic. It deserves special attention, therefore, as a retainer of the heavy metals. But besides its high c.e.c., it not only holds some heavy metals very strongly, but has specific reactions arising from its own chelating ability and the tendency of those metals to combine with the chelating groups.

The chemistry of the organic colloids of soil is still obscure. We assume here, as is commonly done, that while "raw" organic matter is highly variable, the more stable colloidal organic material, into which it has turned over the years in soil, has much in common through the world. This is sometimes called "humic material", a general term which makes no distinction among possible fractions. The source of the negative charge on the colloid is its carboxylate side–chains, together with many phenolic groups which can ionize within the common range of pH; since these phenolic groups which can ionize within the common range of pH; since these phenols are weakly acidic, the c.e.c. of the organic colloid increases substantially between pH 5 and 7. On a few sites some hydroxyls, and

perhaps some imino, groups join with carboxylate in holding suitable metal ions in pentagonal or hexagonal chelate rings. The "suitable" metals are those of the well–known series, $Cu^{2+}>Ni^{2+}>Co^{2+}>Fe^{2+}$, with both Mn^{2+} and Zn^{2+} showing much less chelating tendency than their neighbours in the periodic table.

When the need of plants for Cu and Mn was first recognized, deficiencies were noted on peaty soils and it was believed that the organic matter was responsible for these deficiencies through its chelating power. This belief is questionable for both metals, for Cu, because Cu deficiency in organic soils is cured by adding Cu in amounts as low as one – thousandth of the c.e.c.; for Mn, because Mn^{2+} and Ca^{2+} compete on equal terms on the surface of organic colloid so long as pH is below 6. Yet it is true that Cu is very firmly held by the organic matter, the reason for the apparent anomaly, that the deficiency is easily cured, is probably that Cu can circulate in anionic form.

The soil pH is of importance to the plant availability of the leavy metals, as most of the heavy metals are less available when pH is relatively high, 6.5–7, than under conditions with lower pH. At higher pH levels the heavy metals are bound in almost non–soluble basic salts. Potential toxicity can therefore be reduced by liming.

The plant uptake of heavy metals from the soil depends on a large number of processes and interaction between them. This holds for the availability of the heavy metals and their mobility in soil, the root adsorption of heavy metals and their transport within the plant. Certain heavy metals are taken up more easily than others. This goes for zinc and

cadmium.

Keeping in view the abovementioned discussion, the present investigation was carried out with the following objectives:

1. To find out the content of heavy metals in sewage irrigated soils.

2. To study the distribution of heavy metals in sewage irrigated soil.

3. To study the interaction of added heavy metals in vegetable crops.

4. To study the uptake of heavy metals and their accumulation in vegetable crops.

Chapter II

REVIEW OF LITERATURE

Chapter – II

REVIEW OF LITERATURE

Keeping in view the objectives of present investigation, the available literature has been reviewed as follows:

According to Angelidis and Gibbs (1989), the use of a sequential extraction technique revealed that organic matter and sulfides are the most important carriers of metals in the anaerobically treated sludges. More than 85% of Pb and more than 60% of Cd and Cr were found in this phase. Pardo et al. (1990) reported that town of Volladolid (Spain) was mainly polluted by industrial and municipal effluents which contains Cd, 1.05 and Pb, 18.77 μg^{-1} besides other heavy metals. According to Salim (1990), content of Pb and Cd in sludge varied from 140 to 186 and 5.7 to 9.2 ppm respectively. Industrial waste water rich in heavy metals including Cd, Pb and Cr were also reported by Brij Mohan et al. (1991). Rodger et al. (1992) studied the annual average composition of sewage sludge. According to them, sewage sludge contains Cd (8 mg kg^{-1}), Pb (312 mg kg^{-1}) and Cr(1083 mg kg^{-1}). Adhikari et al. (1993) reported that concentration of Cd, Pb and Cr varied from traces to 3.8, traces to 18.0 and traces to 29.25 mg/kg in sewage effluents and in a sludge content ranged from traces to 10.6; 6.3 to 200.0 and traces to 3523.0 µg/kg for Cd, Pb and Cr respectively.

Jones et al. (1988) had reported distribution of metals in different soil profiles. According to them, content of Cd, Pb and Cr varied respectively from 0.12 to 0.22; 47 to 68 and 115 – 117 mg kg^{-1} (unforested profile) 0.08 – 0.59; 34 – 95 and 35 – 112 mg kg^{-1} (17 years old forested profiles) and 0.08 – 0.88; 5 – 19 and 53 – 148 mg kg^{-1} (32 years old forested profiles). Kakalu (1989) had found large amount of heavy metals in roadside soils. Kuhad et al. (1989b) reported that agricultural soils of Indo – Gangetic plains of Haryana contained 0.50 to 1.25 ppm Cd and 10.0 to 22.5 ppm Pb. According to Grun et al. (1990), soil samples exceeded the threshold value of 0.5 mg Cd/kg soil and concentrations reached > 40 mg/kg soil in some cases. Salim (1990) found that soils of Bahrin (Tubil) contained 242 – 609 μg g^{-1} Pb and 18 – 3.9 μg g^{-1} Cd. Banic et al. (1991) had found large amount of Cd, Pb and Cr in soil examples taken from airport boundaries. Singh et al. (1992) concluded that Cd, Pb and Cr concentration in soil samples collecetd from sites adjacent to carpet industries and motorways varied from 1.94 to 3.66; 8.24 to 22.20 and 1.24 to 2.68 ppm respectively in Varanasi region.

According to Hudai and Sadhu (1990), concentration of total Cd, Pb and Cr were greater in sewage waste water treated soils and decreased as the distance from reference point increased. DTPA extractable contents of these metals (except Cr) were greater in sewage waste water irrigated soils than in tub well water fed soils. Ilangovan and Vivekanandan (1990)

reported that soil irrigated with the effluent year after year contained higher concentration of Cd (19.65 mg/kg soil) and Pb (291.15 mg/kg soil) than the effluent.

Podleasak et al. (1990) had determined Cd content of 824 phosphatic fertilizer samples of East Germany. They found that products manufactured from Kola apatite contained < 2 mg Cd/kg. Other rock phosphate fertilizers contained, on an average 25 mg Cd/kg. As the majority of mineral phosphate fertilizers in the former GDR was produced form Kola apatite, the annual input of Cd into the soil was only = 03 g/ha. Andersson and Siman (1991) had found an increase in Cd levels in soils with increasing rates of fertilizer application. Singh et al. (1992) reported that different fertilizers, viz., calcium ammonium nitrate, urea, superphosphate, diammonium phosphate and suphala (15–15–15) contained 6.50 and 198.0 ; 1.0 and 4.25 ; 185.0 and 601.0 ; 110.0 and 190.0 ; 91.0 and 315.0 ppm of Cd and Pb respectively.

Kuhad et al. (1989a) reported that maximum accumulation of heavy metals was observed in Ap horizon. The values of ratio of metal in Ap versus C horizons indicated the tendency of metal accumulation in the surface horizon. Generally, all the metals including Cd and Pb which were studied decreased with depth. Shuvalov (1989) observed that Cr become more mobile in the soil plant system where Ca was present in the soil. Virgin soils were characterized by lower Cr mobility than in the case of the

cultivated ones. He reported that Cr levels ranged between 0.091 and 0.249 mg/kg in the surface soil layer and 0.0107 and 0.31 mg/kg at 20–30 cm depth. According to Singh et al. (1990), content of lead varied from 7.0 to 9.8 ppm in surface horizons and 1.0 to 5.8 ppm in lower horizons. Khan et al. (1991) studied the effect of some organic pollutants, i.e., methanol, ethanol, propanol, formaldehyde, acetaldehyde, benzaldehyde, acetone, ethyl methyl ketone and cyclohexane in soil. It was found that an increase in the concentration of organic compounds enhances the heavy metal mobility. Sakal et al. (1992) had found maximum concentration of heavy metals in surface layer of soil profile which progressively decreased with increasing depth upto 45 cm and thereafter the decreasing trend was irregular.

Erikson (1989) also reported that water leachable and $CaCl_2$ extractable soil Cd levels were higher in the sand soil than in the clay soil. Fixation of added Cd apparently did not occur continuously at any pH or Cd level, but seasonal variations in solubility and uptake were observed. Eriksson (1990) reported that organic soils generally had higher Cd contents and lower pH levels than mineral soils. Hirsch and Banin (1990) observed that free Cd^{2+} and $CdHCO^{3-}$ were each estimated to constitute 35% to 45% respectively of total soluble Cd in the calcareous soil solution, which had pH values between 7.5 and 8.5. Organo–Cd complexes were shown to be present in relatively minor amounts in these soils.

Misra et al. (1990) had studied the transformation of added heavy metals under flooded condition. According to them, extractability of Cd was the highest and Cr(vi), the least in soils upon initial flooding. The reversion of Pb into non extractable form was relatively slow. The metal of Cr(vi) was reverted to non–extractable form very fast even of 120 days of flooding. Yong et al. (1990) found in their experiment that high carbonate content in the illite gave it a higher buffer capacity than smecite and natural clay, and permitted it to higher buffer capacity than smectite and natural clay, and permitted it to retain higher amounts of Pb. High Pb uptake by the clays can affect the buffer capacity and Pb retention capacity. Elkhatib et al. (1991) reported that the highest adsorption capacity was exhibited by $CaCO_3$ rich soil (773.55 m mol Pb kg^{-1}). Raising the temperature from 298 K to 308 and 318 K increased the sorption capacity of soils. According to Mira Das (1991), the transformation of added Cr(iii) and Cr(vi) was influenced by Fe_2^+, Fe_3^+, Mn_2^+ and Mn_4^+ with or without glucose addition under varying periods of flooding was studied in an inceptisol, vertisol and ultisol. Results showed that the concentration of Cr(vi) in soil solution decreased with flooding and further in presence of glucose and Fe_2^+. The ability of these soils to reconvert soluble to an unavailable form was in the order of vertisoil > inceptisol > ultisol. Xiong and Lu (1991) reported that heavy phosphate application to a submerged red earth inhibited the transformation of exchangeable Cd to less available Cd forms.

Kuo and McNeel (1984) reported that sorption of Cd on synthethic hydrous ferric oxide was positively related of pH. Kuo et al: (1985) used regression analysis and found that exchangeable Cd in a sludge amended soil was positively related to total soil Cd and negatively related the soil pH and Fe–oxide. Baghdady (1987) stated that increase in total Cr content was found with higher pH, $CaCO_3$, CEC and clay content. Increasing pH and $CaCO_3$ gave a decrease in Cd and Pb content, while, a higher humus content gave an increase. Cd and Pb were closely correlated with pH but only total Cr content was significantly correlated with $CaCO_3$, humus and clay content. Eriksson (1989) reported that soluble fractions of Cd increased as the pH was lowered. Kuhad et al. (1989b) reported that Pb content was positively correlated with pH and Cd. Xian and Shokhifard (1989) noticed that when pH values were decreased from 7.0 to 4.55, levels of Cd and Pb in exchangeable form increased, decrease in carbonates and slightly in Fe–Mn oxide forms. According to Erikson (1990), in mineral soils the amounts of soil Cd extractable in 2M HNO_3 was positively correlated with pH and the contents of organic matter and clay. Andersson and Siman (1991) reported that liming consistently decreased easily soluble fractions of Pb in soils. According to Basta and Tabatabai (1992), at high concentrations, metal adsorption by soils was strongly related to soil pH and metal adsorption increased with increasing solution pH. A decrease in solution pH with increasing initial metal concentration was also observed.

Sakal et al. (1992) had found significant and negative correlation of Cd and pH and positive with organic carbon and clay content of the soil.

Kuo and Baker (1980) found that the presence of Zn and Cu in solution reduced Cd sorption. They also hypothesized that reduced sorption Al and Mn. Christensen (1987a) reported that other heavy metals like Ni, Co, Zn, Cr, Cu and Pb compete for Cd sorption sites. Competition decreased the Cd distribution coefficient 2 to 14 times. Zn was accounted for most of the observed competition with Cd. Competition for Cd sorption sites was observed in top soils as well as in sub soils. Christensen (1987b) in his another study reported that Cd distribution between soil and solute decreases for increasing Zn solute concentrations. The competition of Zn was governed by the product of the Zn soil sorption stability constant and the actual Zn solute concentration.

According to Ajmal et al. (1990), the ranges of concentration of metals in water of the Ganga river (Naroora to Kannauj) were found as follows:- Cd, 1.8 to 11.8 and Pb, 82.9 to 299.1 µg−1. Whereas, sediment contained 2.7 to 4.5 µg−1 cd and 20.27 to 547.80 µg−1 Pb. Studies of Hasan (1990) revealed that Pb and Cr were alarmingly high in river water due to discharge of tannery wastes in the river. The levels of heavy metals in well waters were comparatively lower. Israili et al. (1990) has analysed water of river Ganga at Kanpur and found 0.001 – 0.025

ppm Cd: 0.005 – 1.29 ppm Pb and 0.001 – 1.21 ppm Cr. Joshi (1990) reported that Hooghly estuary contained 0.0 – 3.1, 0.0 – 1.8 and 0.0 – 1.02 μg^{-1} of Cd, Pb and Cr respectively. Kakati and Bhattacharya (1990) had found appreciable concentrations of Cd, Pb and Cr in surface water of Greater Guwahati. Nand Kumar et al. (1990) determined the chromium content of water resources near a chromate factory in Ranipet. They found that total chromium in irrigation wells and reservoirs ranged from 10 – 465 ppm and abandoned wells 60 – 1200 ppm.

Palmer et al. (1990) reported that status of Cr(vi) in a shallow aquifer varied from 10 mg/l to 19 g/l in the ground water of the lower aquifer. According to Pardo et al. (1990), sediments taken from Pisuerga river (Spain) contained 1.05 μgg^{-1} Cd, and 18.77 μgg^{-1} Pb. Prasad and Rupainwar (1990) had determined status of heavy metals in the bank sediments of river Ganga in Varanasi and Mirzapur city regions. The average values for the metals in the sediments at Varanasi were found to be in the order of Fe>Mn>Zn>Cu>Ni>Cr>Cd>Pb and for Mirzapur the order was Fe>Mn>Zn>Ni>Cu>Cr>Cd>Pb. Singh et al. (1990) reported that the content of chromium varied from 1.1. to 32.3 ppm in different water resources of carpet industrial belt (Bhadohi, Gopiganj) of Varanasi. Trapathi et al. (1990) reported that the heavy metal concentrations of K.D. pond, Unano (U.P.) varied from 0.001 to 0.04 ppm Cd; 0.49 to 1.61 ppm Pb and 0.05 to 0.25 ppm Cr. Study of Ihenyen (1991) revealed that concentration of

Pb and Cr were proportionally high in sediments along high density motorways while, lower concentrations were found along medium and light density motorways. Singh et al. (1991) stated that water samples taken from area adjacent to motorways contain higher amount of Pb (0.2 to 19.6 ppm) than those away from motorways (0.1 to 1.5 ppm) in Varanasi. They also reported that water samples taken from carpet industrial belt contained large amount of Cr than the non–carpet industrial belt. Content of Cr varied from 0.2 to 35.0.

Water samples collected from the various sources that are used in drinking water supply, were analysed for trace and toxic heavy metals like Cd, Pb and Cr besides other metals by Wadhwan et al. (1991). According to them, 30% of the samples collected from hand pumps were found to had more lead (0 – 1.19 ppm) and 15% of the samples had more Cd (0 – 0.04 ppm) as compared to WHO/ICMR recommended safe limits. Further, open well, tube well and open canal were found to contain less amount of metals. Garg et al. (1992) reported that water samples of river Ganga et al. (1992) reported that water samples of river Ganga at Kanpur contained 8.8 to 41.4 μg/l Pb and 10.7 to 225.5 μg/l Cr.

According to Rodger et al. (1992), sediments collected from the sea bed accumulated large amount of Cd and Pb. They also reported that about 18 – 20% of the Cd and Pb in sediments was due to sludge disposal. Singh et al. (1992) had determined

the status of Cd, Pb and Cr in different water resources adjacent to carpet industries in Varanasi region. They found that contents varies from 0.79 to 3.20; 7.45 to 24.43 and 1.50 to 16.0 ppm for Cd, Pb and Cr respectively. Totawat (1992) had studied the ground water pollution adjoining zinc smelters effluent stream in Rajasthan. He found that in general the cadmium content of water from the wells was higher than value permissible from the view point of health significance (less than 0.005 mgL^{-1}; WHO, 1982). Further, the water samples collected from the wells which were located within 80m vicinity of the effluent stream/river carrying the effluent onward, contained the Cd level much higher than limit permissible (0.01 mgL^{-1}), for the irrigation water.

Nag and Das (1993) suggested that drinking water quality of Hooghly district appeared to be not very safe all over the district due to presence of Cd with other heavy metals beyond their permissible limits.

Watanabe et al. (1989) reported that rice samples collected from 15 areas of Asia contained Cd and Pb with a geometric mean of 20.0 mg g^{-1} and 15.7 mg g^{-1}. Cary and Kubota (1990) revealed that plant samples taken from plants growing on high Cr soils contained higher concentrations of Cr than similar plants growing on low Cr soils. Kumar et al. (1990) reported that Cr ranged from 67 – 200 ppm in paddy hay, 30 – 35 ppm paddy husk and 1 – 2.8 ppm in rice samples collected from areas adjacent to a chromate factory. Alegria et al. (1991) pointed out that the lead

content of soils was not main factor that influenced the lead content of vegetables. Anthropogenic and environmental factors played a more important role than lead in soils in respect of lead content of vegetables. Singh et al. (1992) reported that in grasses, content of Cd, Pb and Cr in ppm varies from 0.30 to 24.22 ; 2.24 to 82.23 and 0.42 to 21.40 respectively in polluted area and 0.01 to 0.42 ; 0.11 to 0.76 and 0.01 to 0.36 in non-polluted area respectively.

Lehn and Bopp (1987) cultivated five plant species on a soil polluted by the emissions of Cement plant. They found that Cd was taken up by roots whilst Pb was deposited mainly on the plant surface. However, during cultivation in winter months, a remarkable deposit of lead via the roots was found. Further, during the life time of a plant concentration of Cd was always highest in the seedlings. The decrease in metal concentration with maturity depend upon the plant species and the element. Curzydlo (1988) found in his study that the straw of cereals contained much more heavy metals (Cd and Pb) than in grains. In potato tubers, there were more heavy metals in the peel than in the flesh, while in mangolds and parsley more heavy metals were found in the leaves than in roots. According to King (1988b), Cd concentration was maximum in the lower leaves and decreased with leaf position up the stalk in tobacco. Wallace (1989b) reported that Pb and Cr were mostly accumulated in roots with very little in shoots, whereas, substantial quantity of Cd was also

in shoots. According to Dani ad Dara (1990), Cd accumulation in different parts of the barley plant was in the order of root > leaf > stem. Gupta and Potalia (1990) reported that grain contained less Cd in comparison to straw.

Singh et al. (1992) found in their study that Cd, Pb and Cr were accumulated most highly in the root than stems and leaves. Lehn and Bopp (1987) in their study found that Cd uptake was upto 10 times higher in dicots than in monocots. Uptake of Cd by perenial ryegrass (Lolium perenne) and winter rape (Brassica rapus) were studied by Erikssson (1988). He observed that the crop Cd concentration in rapeseed generally was 3 to 5 times higher than in the ryegrass. The higher uptake in rapeseed was due to genetic differences and probably also higher water uptake. The more leafy rapeseed had a higher water consumption than reygrass. Eriksson (1990) in his another study reported differences in Cd content between varieties of oats and winter wheats. Sauerbeck (1991) reported that most dicotyledons plants absorbed more heavy metals than monocotyledons. An exception was ryegrass which absorbed Ni unusually in large amounts.

Dani and Dara (1990) studied the effects of different levels of Cd and growth of barley plant. It was observed that there was a linear increase in concentration of Cd in plant tissue with the increasing soil cadmium. Further, with increasing levels of Cd in soil, germination, shoot length and root length decreased linearly by 29%, 65.6% and 78.8% respectively when Cd in soil was 237

mg/kg. Prasad and Prasad (1990) found in their study that lead inhibited porphyrin biosynthesis significantly in the germinating seeds of bajra. Both 5–aminolevulinic acid dehydratase and porphobilinogen deaminase activities were inhibited by lead. Chlorophyll "a" and "b" and total chlorophyll contents in dark grown seedlings were also significantly decreased, suggesting the impairment of chlorophyll biosynthesis by Pb in germinating seeds.

Rashid et al. (1990) observed that treatment with different doses of lead nitrate resulted in marked reduction in periclinal and anticlinal dimensions of epidermal cells of leaf and stem, length and breadth of the stomata and enlargement in the area of pith hollowness over the control. Sehgal and Rattan (1990) found that higher the dose of added Cd, higher was the reduction in yield of grain and straw of peas in acid soil, grains were not formed when the dose of Cd was more than 10 ppm. They also showed that Cd content in the grain and straw of peas increased with applied Cd, the extent of increase was much more in acid soil than in alkaline one. Singh and Nayyar (1991) reported that growth of wheat crop decreased with an increase in rates of Cd application. Phytotoxic symptoms on wheat were also observed. Furthermore, grain and straw yield decreased due to Cd application. Concentration of Cd in leaves, grains and straw of wheat increased significantly with addition of Cd. They suggested that the decrease in wheat yield was due to the

consequence of the toxic effect of high levels of Cd in plant tissues.

According to Agrawal et al. (1981), plants near the roadside had higher Pb concentration than at a distance of 4 – 6 m. High values of metal accumulation in plants located near highways were observed by Albasel and Cottenie (1985). According to Rekha et al. (1985), analysis of washed and unwashed leaves have shown that lead content in the plants from the traffic area was high ranging from 29 μg/g to 185 μg/g as compared to the control, where, it ranged from traces to 20 μg/g. Washed leaves contained less amount of Pb than the unwashed one. Analysis of cedar bark samples and deposition samples in the Nagatcuta area (Japan) showed contamination by Cr and Pb was indicated by enrichment factor values ranging from 2 to 361, particularly adjacent to the highways. It was suggested that motor traffic was the major source and contamination occurred primarily by aerial deposition. There was a negative correlation between heavy metals levels and distance from the road (Nyangbabo and Ichikeeni, 1986). Banic et al. (1991) found that plant samples collected from the airport's boundaries had greatest content of Cd, Pb and Cr.

According to Koning (1986), industrial emissions markedly increased Cr content of sugarbeet leaves and roots and herbage regrowth. Wadge and Hutton (1986) found that barley and cabbage plants grown in green house on soil amended with refuse

incinerator fly ash contained significantly elevated levels of Cd and Pb. Cd uptake was the greatest in both plant species. Cabbage grown on 20% ash amended soil contained 146 times more Cd than controls. Cd and Pb concentrations (μg^{-1} dry wt.) were 6.3 to 33.0 and 21.6 to 81.8 (barley leaves) ; 21.7 to 71.6 and 1.2 to 15.9 (cabbage) respectively. Singh and Keffer (1989) reported that Cd concentrations in the edible parts of plants from sludge treated plots were usually less than 1.0 m kg^{-1}. In radish leaves, from plots receiving a sludge with 20 mg of Cd kg^{-1}, Cd was present at 4, 2, <1, <1 and 2 mg kg^{-1} for the years 1, 2, 3, 4 and 5 respectively. Thus, some Cd became available to crops during the fifth growing season. Grun et al. (1990) had determined the content of Cd in samples of maize and grasses collected from a field affected by sewage effluent disposal. They reported that maize had higher Cd concentration that grasses with 18% and 38% of the samples respectively showing concentrations < 0.3 mg/kg dry matter. Maximum concentrations of 14 and 8.1 mg/kg dry matter were found in maize and grasses respectively. According to Singh et al. (1991), significant reduction in dry matter yield of berseem crop was recorded by refinery effluent irrigation. Further, contents of heavy metal increased with increasing level of irrigation with sewage water as well as refinery effluent. Content of Cd, Pb and Cr were 0.19 – 0.84 ; 37.2 – 61.3 and 3.9 – 4.4 ppm respectively. Srikant and Reddy (1991) determined the lead, cadmium and chromium content of vegetables grown in urban sewage–sludge of

Hyderabad (India). According to them, concentration of Pb in leaves was high reaching upto 22.5 mg/kg in spinach. Maximum concentrations reported were 4.75 and 9.67 mg/kg for cabbage and spinach respectively. Tadesse et al. (1991) reported that sludge application increased the plant tissue concentration of Cd along with other heavy metals.

Jensen and Hans (1990) carried out a pot experiment with two soils which had not been exposed to atmospheric deposition or any other pollution with Cd during the last 200 years. The experiment showed that about 1% of the plant Cd originated from the fertilizer and the availability of newly added Cd was similar to that of the indigenous Cd in the soil with respect to plant uptake.

Ramachandran et al. (1990) working with rice found that rock phosphate application enhanced Cd and Pb content of rice grain over the control. Andersson and Siman (1991) reported that Cd was influenced by the level of fertilizers with an obvious tendency towards increasing Cd levels in plants at increasing rates of fertilizer application.

According to Eriksson (1990), in winter wheat the presence of Zn reduced the Cd uptake and vice–versa. According to Gupta and Potalia (1990), Zn application in conjunction with Cd counteracted the depressing effect of cd in respect to yield and Cd concentration of wheat. The effect of Si(OH) on Cr toxicity and elemental concentrations, in ryegrass were studied by

Otabbong (1990). He observed that Cr toxicity was increased by the Si. The increase in toxicity was accompanied by a higher Cr uptake due to silicon's ability to inhibit the reduction in plant tissue of the highly toxic or Cr^{6+} anion to the less toxic Cr^{3+}.

According to Singh and Nayyar (1991), concentration of Zn in wheat increased with Cd application. The increased Zn concentration in plant with Cd application might have arisen due to greater dissociation of Zn from the binding sites due to competition for the same sites. Thus, increasing Zn concentration of Fe in wheat tended to increase with rates of Cd application. They concluded that the reduced growth with Cd application had contributed towards higher content of Zn and Fe in plants. Xiong and Lu (1991) suggested that Cd uptake by rice plant increased with increasing P supply but plant resistance in Cd also increased at high P level.

Merry et al. (1986) were able to show that lead concentrations of the radish and silver beet plants decreased with increasing soil pH, the effect was more marked in highly contaminated soils. Obviously, calcium carbonate applications increased the yields and decreased the concentration of Pb in both plants. On the other hand, sulphur treatments (Gypsum, as compared to control decreased the yield and increased lead concentration in both radish and silver beet. According to Dahiya et al. (1987). Cadmium reduced the corn plant growth, significantly decreased the yield and increased the concentration

of Cd, and N but decreased the concentration of P, K and Na when applied singly. Whereas, in combination with FYM dry matter yield. Content and uptake of N, P, K and Na increased. Application of FYM also decreased the concentration of Cd in plant but increased the uptake because of less availability of Cd due to binding and chelating capacity of FYM. Increased uptake was due to increased dry matter production. Eriksson (1988) reported that the addition of organic matter reduced the plant uptake of Cd and showed a greater ability than clay to adsorb Cd. Further, addition of organic matter reduced plant uptake more efficiently in sand than in clay even though the exchangeable Cd did not differ between two soils. Increasing clay content had not significantly decreased plant uptake. King (1988a) reported that lime reduced the effect of Cd loading rates and soil types on concentration in tobacco.

According to Eriksson (1989), increasing the pH from 5 to 7 by adding CaO invariably reduced the Cd content of ryegrass plants but this decrease was less constant where the pH had been increased only by 6. In some cases, acidifying the soil with sulphur to reach a pH of 4 also led to a decrease in plant Cd content. Otabbong (1989) noticed that KH_2PO_4 was able to counteract the toxic effect of CrO_3, applied at low rates, by increasing the P concentration in ryegrass tissues. Benedetti et al. (1991) also reported that Cr toxicity in plants was greatly decreased by application of KH_2PO_4 at rates not exceeding 400

kg/ha. Sarkunan et al. (1991) had studied the effect of compost. Lime and P on cadmium toxicity in rice. .They found that accumulation of Cd in grain above permissible level (1 ppm) occurred only at 200 ppm of Cd addition, irrespective of the nature of amendments. They observed that lime had depressing effect on Cd content in both grain and straw at higher levels of Cd addition as against enhanced Cd content in case of P treatment. They concluded that the beneficial effect of lime in counteracting the Cd toxicity may be attributed to the decreased solubility and mobility of the metal in soil.

Singh et al. (1992) reported that growth and production of wheat was normal upto 250 ppm of Cr in the presence of pyrites. Furthermore, the amendments of soil with pyrites reduced the uptake of Cr by roots, shoots and grains. According to them, pyrites (Fe^{2+}) causes conversion of available Cr(VI) (more toxic) to relatively unavailable Cr(III) (less toxic). Singh et al. (1992) reported that the depressive effect of Cd on dry matter yield was less in presence of FYM. The concentration and uptake of Cd in plants increased with increasing rate of Cd and N and FYM decreased it at all Cd levels. The affect of Cd on concentration of N was antagonistic and the antagonism to some extent was overcome in presence of FYM.

Narwal et al. (1992) conducted a field experiment in a barren soil (due to excessive irrigation with industriaesal effluent in Northern India) was amended with 0, 0.25, 0.5, 1.0

and 2% farmyard manure, and test crops. Application of farmyard manure significantly (p<less than >0.05) decreased the Ni and Cd contents in all four crops. Nickel uptake in the heavy polluted soil was in the order: carrot <more than> spinach <more than> fenugreek <more than> wheat.

Dang et al. (1990) reported that onion (Allium cepa) and fenugreek (Trigonella foenum–graecum) growth was measured in a glasshouse on a slightly alkaline clay–loam soil from Northern India. Cd, Ni, Pb and Zn were applied at 0, 50, 100, 200 or 400 mg/kg of soil. The FW and DW of both crops were drastically reduced even at the 50 mg addition of Cd, and decreased further at higher levels. There was a slight decrease in the yield of both crops at 50 mg Ni but at 100 mg Ni and above the decrease was significant; no growth was observed at 400 mg Ni. The application of 50 mg Zn slightly increased yield of both crops but the yield, particularly of fenugreek, decreased at higher levels of applied Zn. The threshold concentration, toxicity index and loading rate of produce 10% yield reduction were also calculated. These value suggested that the toxicity of heavy metals varied with crop species. The concentration of the elements in onion bulbs, and fenugreek roots and leaves increased linearly with increasing levels of applied elements. The uptake of Zn was highest, followed by Cd, Ni and then Pb. The roots accumulated higher amounts of these elements than the leaves. Tissue concentrations of Cd, Ni, Pb and Zn associated

with 10% yield reduction of for onion were 6, 3.2, 8 and 75 ppm., respectively; for fenugreek, the concentrations were 1.5, 7.8, 11.5 and 54.5 ppm., respectively. In general, phytoxicities were found to be in the order: Cd > Ni > Pb > Zn. The DTPA extractable elements in soils, after the harvest of crops, increased with increasing levels of applied elements.

Karagiannidis (1999) studied the use of an industrial solid waste that contains manganese dioxide (MnO_2) in two years field trials in Greece. This waste is neutralized with slaked lime. Chemical analysis indicated that it has pH 7.9 and contains total Mn 14.12%, high levels of Al, K, Ca, Fe but lower levels of heavy metals such as Cu, Zn, Co, Cr, Ni, As, Cd and Sn. The solid waste amounts added to the soil one year before the beginning of the study were 0, 400, 500 and 600 t ha^{-1}, while the experimental plants used for the following two consecutive years were maize, sunflower, cotton and tomato. The results showed that the addition of 500 and 600 t ha^{-1} of waste to the soil improved maize production by 8.1 fold and sunflower seed yield by 4.0 fold. The 1000 grain weight was more than doubled. The cotton fibre and tomato production improved up to threefold. The favourable effect of the solid waste on the cotton and tomato production was weaker during the second growing period. The concentrations of the various nutrient elements and heavy metals in the plant are tabulated.

Gorlach (1994) conducted a pot experiment with 10 test plant species reported that liming decreased heavy metals uptake

by radish, sunflower, hemp and clover (Trifolium) in the following order: Zn > Ni > Cd > Cu > Pb. Grasses were lest affected.

Madhavi and Charyulu (1998) studied the toxic effect of different concentrations and combinations of the heavy metals lead, cadmium and mercury, and the role of chelating agents like EDTA, gypsum and serpentine soil singly and in combinations in reducing the toxic effect of heavy metal on the growth and metabolism of Trigonella foenumgraecum, were investigated. The sub–lethal, toxic and lethal concentrations and LD50 varied for different heavy metals. Germinations was totally inhibited at 500 μM Pb while it was drastically reduced at the same concentration for Cd and Hg. The radical growth and root elongation were drastically reduced with the increasing concentrations of Pb, Cd and Hg. Heavy metals in different combinations reduced root development, thereby increasing the shoot–root ratio. The toxic effects were more pronounced in earlier than in later growth. The levels of chloroplast pigments Chl–a, Chl–b, carotenes and xanthophylls decreased with the increasing concentration of Pb, Cd and Hg. Maximum toxic effect was shown by Pb + Cd + Hg. Transpiration and stomatal conductance were reduced. Maximum reduction in transpiration was caused by Pb + Cd + Hg treatment. In vivo photosynthesis was reduced with increasing concentrations of Pb, Cd and Hg, with maximum reduction in Pb + Cd + Hg treatment. The use of

EDTA, gypsum and serpentine soil either singly or in combinations reduced the toxic effect of Pb, agents showed protective effects on chloroplast pigments.

Joseph et al. (2001) reported that "In order to assess the contamination of heavy metals and pesticides in water and sediments, water samples from Kandereru creek (near Krishnapatnam and Pudiparthi villages), tasparc pond and bore well (Pudiparthi village) and Krishnapatnam ponds of Nellore District (Andhra Pradesh) and commercial farm pond and sea water of Tuticorin area of Tamil Nadu were collected during March – April 1993 and analysed for heavy metal and pesticides concentration. Sediments samples were collected from Kandaleru creek and ponds soils of shrimp farms at Pudiparthi for heavy metal analysis. The concentration of heavy metals and pesticides were below detection level of instruments except for zinc and mercury. Zinc was in detectable level in Tasparc bore well water (0.38 mg/l) and Kandaleru creek water (1.35 mg/l). Low level of mercury concentrations were noted in influent sea water at Tuticorin farm and Krishnapatnam creek water. Sediment samples registered the occurrence of all heavy metals except cadmium and mercury in pond and creek sediments and their concentration in creek sediment is not much as compared to pond sediment presuming that there is no contamination of the creek by metals from aquaculture activities."

Sadanandan and Hamza (2001) reported that "Investigations were carried out at the Indian Institute of Spices

Research, Calicut, Kerala in a laterie soil (Ustic Humitropept) for 12 years to study the effect of continuous applications of rock phosphate. Mussoorie rock phosphate was applied at 3 levels (40,80,120 kg ha^{-1}) for black pepper (*Pipper nigrium L.*) The effect was compared with conventional sources of P, Super phosphate and Bone Meal each applied at 3 levels. There was an absolute control. The heavy metal residue due to rock phosphate application was studied. The heavy metal content in the leaf tissue and pepper berry was evaluated over the year. Studies showed that continuous application of mussoorie rock phosphate did not significantly increase the concentration of heavy metal viz., Fe, Mn, Zn, Cu, Al, Cd and Cr either in the soil or in the leaf or in pepper berries. Application of Mussorie rock phosphate @ 80 kg P_2O_5 ha^{-1} did significantly increased the yield of pepper by 20% over single super phosphate. The benefits/cost analysis showed that application of Mussoorie rock phosphate in economical that super phosphate."

Pradhan et al. (2001) reported that "Raw domestic sewage water from *Avas Vikash Colony*, Pratapgarh having pollution of about 2000 was utilized for irrigation of agricultural crops like wheat, blackgram, mustard and paddy at Sunnhemp Research Station, Pratapgarh. Response of the raw sewage water on the crop yield was at par with the normal irrigation with tube well water. In case of paddy the response was better when irrigated with sewage water. Analysis of sewage water indicates low

content of nitrogen, phosphorus and organic load whereas calcium, magnesium and chlorides are high in concentration. As B.O.D. of raw sewage water was low there are possibilities of fish culture with the available sewage water after minor treatment in the setting tanks for which no elaborate arrangement is required. Moreover, the raw sewage water also contains nitrogen, phosphorus and organic matters, which not only improve the soil health but also encourage the crop growth too. In view of the above, there is scope to study the effect of high concentration of chlorides. Calcium and Magnesium on the soil health vis–à–vis growth of crops and fish as well."

Sewage sludge where available is applied to the agricultural soil as a source of nitrogen to crops. The most determining factor is the N supplying capacity of the sludge applied. Sludge contains 50 to 90 percent of N in organic form (sommers 1977) and can be considered a potentially valuable fertilizer (Biswas Mukherjee 1990). This study was planned to investigate the N–mineralization potential (No) and rate constant (k) of four different soils treated with various levels of sewage sludge.

Raw sewage and sludges depending upon their sources, may contain as appreciable amount of metallic micronutrients and heavy toxic metals. Long–term application of these materials on cultivated lands may cause accumulation of heavy metals in soil and may become toxic to plants. In this note, the heavy

metal contents of the Calcutta sewage effluents and sludge as well as contents of these metals in the soils receiving in sewage and sludge are reported.

Cadmium is a non–essential element in plant nutrition under normal condition, plants take up small quantities (< 1 mg kg^{-1}) of Cd from soils (Fleischer et al. (1974)) but in areas of suspected Cd contamination the plant levels may be much higher than 1 mg kg^{-1}. Increased Cd contents of soils have been associated with reduction in plant growth, measured as dry matter yields (Haghiri 1973; Binghanm et al. (1975)). Plant Cd level, which should be known in order to assess the hazard is affected by many factors, i.e. soil properties (including Cd content) and climatic conditions. Plant factors, such as species and cultivars also exert marked differences with regard to Cd accumulation and tolerance by Plants (Miles and Parkers 1979).

The indiscriminate disposal of sewage sludge and city waste containing domestic and industrial effluents on agricultural lands is a major source of heavy metals causing soil pollution. The continuous use of these wastes by farmers in the areas adjoining sewage sludge plant has become a common practice which results in the accumulation of heavy metals in soils to such a level that may become Phytotoxic (Kirkham 1983) and eventually be hazardous to animals and human health offer entering in their systems through food chain.

The concentration of extractable Cd declined with increasing distance from the sewage sludge disposal point and

with the amount of sludge and sewage water application in soil. The Trend is more or less similar to Pb regarding depthwise distribution. In some of the soil profiles, sub–surface layers contained similar a slightly more extractable Cd then their surface layers. This downward movement of Cd from surface may be ascribed to the formation of soluble metal soil organic mater complexes as reported by Lung et al. (1976).

Joshu et al. (1998) reported that dewatered biosolids (DWB) were applied at 0–120 dry t/ha to 3 types of soils in a sheep grazing trial at Goulburn over a period of 1.5 years data were gathered on the surface and subsurface movement of nutrients and metals in the runoff water and soil profile, respectively. The biosolids reduced runoff and increased surface retention of rainfall. Data show environmentally insignificant concentrations of metals in the runoff waters whereas nitrate concentrations were significantly greater compared with control plots. Zinc and copper moved in the upper 30 cm of the soil profile, whereas nitrates moved down the soil profile to a depth of 50 cm in the duplex soils and 70 cm in the sandy red earth. Subsurface lateral movement of nitrates was observed in one duplex soil on the 60 and 120 dry t/ha treatments and was significant in the higher rate. Surface and subsurface movement of nitrate and some metals were detected in the trial. However, the actual amounts of these plant nutrients were low and almost negligible in treatments applied at rates of 30 dry t/ha.

Moolenaar and Beltrami (1998), studied the Applications of sewage sludge and Bordeaux mixture (Bm) (a mixture of copper sulfate and lime) add heavy metals to the soil. At an experimental farm in the Cremona district (Italy), current heavy metal contents in soil and their removal via harvested products were measured. Heavy metal adsorption by soil from this farm was also measured. With these data projections were made of the long–term development of heavy metal (Cd, Cu, and Zn) contents in soil, crop removal, and leaching at different application rates of sewage sludge and Bm. These projections were compared with existing quality standards of the European Union (EU) and Italy with regard to soil and groundwater. The calculations show that the permitted annual application rates of sewage sludge and Bm are likely to result in exceedance of groundwater and soil standards. Sewage sludge applications, complying with the Italian legal limits, may pose problems for Cd, Cu and Zn within 30, 70 and 100 years, respectively. Furthermore, severe Cu pollution of integrated (mildew controlled by Bm and organopesticides) and especially organic (Bm only) vineyards is unavoidable with the currently allowed application rates of Bm. The results suggest that the current Italian soil protection policy as well as the EU policy are not conducive to sustainable heavy metal management in agroecosystems.

Csillag et al. (1996) conducted that, batch experiments on samples of the A horizon of a coarse–textured, slightly acidic

brown forest soil in order to study the impact of metal loading rate, soil water content, adsorption time and soil acidification on the release of Cd, Cr, Ni, Pb and Zn into the soil solution. The metals were applied either as multicomponent nitrate salt solution or as metal–enriched sewage sludge. The soil loading rates were in the following order: Cd < Ni < Cr=Pb < Zn. The liquid phases of unloaded, loaded and loaded + dried + acidified soil samples were obtained by centrifugation using a rotor speed corresponding to −1500 kPa (conventional wilting point of plants). Cadmium, Ni and Zn entered the liquid phase in relatively higher amounts than the less mobile Cr and Pb as related to their previous loading rates. Much higher adsorption was found in the sludge than in the soil with the exception of Ni. Chromium and Pb were adsorbed by the sludge to such a high extent that their adsorption hardly increased when the metal enriched sludge was added to the soil. While element concentrations in the soil solution after the acidic treatment were generally proportional to the previous loading rates, with the exception of the strongly adsorbed Cr (Cd < Cr < Ni < Pb < Zn), the recoveries expressed as percentage of the applied amounts reflected the order of the element mobilities (Cr < Pb < Ni > Cd > Zn). The results indicate that considerable release of metals into the soil liquid occurs only under extreme conditions (excessive metal contamination and strong acid pollution).

Sloan et al. (1996) the objective of this study was to quantify percent recovery of biosolids–applied heavy metals in a

well – drained soil. Three annual applications of biosolids resulted in cumulative biosolids loading of 0, 60, 120 and 180 kg/ha. Cumulative metal loading for the 180 kg/ha biosolids rates were 25, 141, 127, 43, 173 and 348 kg/ha for Cd, Cr, Cu, Ni, Pb and Zn respectively. Soils were sampled to a depth of 0.9 m. Soil organic carbon (OC) was measured. Soil was extracted with 1M HNO_3 and metals were determined in the supernatants. Soil OC concentrations were linearly correlated to biosolids loadings and did not change significantly during the 16 year after biosolids applications. Concentrations of extractable Cd, Cr, Cu, Ni, Pb and Zn in biosolids – treated soils were much greater than the control to a depth of 0.30 m ($P < 0.01$), slightly greater at 0.30 to 0.45 m ($P < 0.05$) and same as the control below 0.45 m. For the 180 kg/ha biosolids loading, percent recoveries for Cd, Cr, Cu, Ni, Pb ad Zn were 112, 59, 119, 114, 102 and 97%, respectively. Low recovery of Cr was probably due to incomplete extraction from the soil. These results show that complete recovery of biosolids applied heavy metals is possible when plot size is large enough to prevent cross – mixing of treated soils during tillage operations and when sediments losses are minimal.

According to Berti and Jacobs (1998) the horizontal and vertical distribution of trace elements as a result of the application of sewage sludge at phytotoxic levels was studied in the profile of a cropland soil (Metea sandy loam; loam, mixed, mesic Typic Hapludalf). Municipal sludges containing high

concentrations of Cd, Cr, Cu, Pb, Ni and Zn were applied to cropland from 1977 to 1986 at three rates plus an untreated control. Total elemental analysis of soils collected in 1989 and 1990 indicated that lateral distribution of trace elements had occurred. This lateral distribution was most likely a result of the physical movement of soil particles with agronomic operations. The elements, however, were not distributed below the sampling depth of from 15 to 30 cm. Mass balance calculations resulted in average trace element recoveries that ranged from 45 to 155% of the total applied. These calculations were highly variable, indicative of the highly variable nature of sludge composition, lack of total uniform sludge applications, soil movement due to tillage operations, and sampling method. Because of the potential errors associated in mass balance calculations, recoveries that have been calculated in this and other studies that deviate substantially from 100% should reasonably be expected. Direct examination of the relatively few ways in which trace elements are lost from a soil (i.e., plant uptake, soil movement via tillage, water and wind erosion and deep leaching) may be more meaningful than mass balance calculations to be determine the fate of trace elements applied to soil.

Mitra and Gupta (1999) reported that the nutrient and heavy metal status of sewage irrigated soils from a vegetable growing area close to Calcutta was compared with non–sewage (tubewell water) irrigated soils of Baruipur, India, during both

the monsoon and winter seasons. The quality of effluent from sewage channel and groundwater from tubewell was suitable for irrigation although they differed widely of their chemical characteristics. A high pH and accumulation of salts were common in sewage–irrigated soil. Enrichment with organic matter, nitrogen and phosphorous was comparatively higher in sewage–irrigated soil as compared the tubewell water irrigated soil. Total Fe, Cu and Zn concentrations were much less in tubewell water irrigated soil. Copper and Zn concentrations were above the normal range in sewage irrigated soil. Concentrations of Pb, Cd and Cr were above the permissible limits in sewage irrigated soils. In most of the cases concentrations of macro and micronutrients were higher during the winter than those during the monsoon.

Colombo et al. (1998) reported that a field experiment on a silty loam Cambisol in northern Italy was performed on a 3–course rotation (maize, sugarbeet and wheat) amended for 8 years with 7.5 or 15 t/ha of liquid, dewatered or composted sewage sludge. Cu, Zn and Ni were determined in soil layers at depths of 0–30, 30–60, 60–80 and 80–100 cm. Trace elements showed a moderate tendency to migrate below the amended layer. Heavy metal mobility was particularly evident when using DTPA – extracting solutions rather than the HNO_3 + $HClO_4$ mixture.

Li–QuoXue; et al. (1998) stated that, a greenhouse experiment was conducted with Chinese cabbages (B. chinensis

[B. pekinensis?]) to evaluate the bioavailability of heavy metals from a metal–enriched sewage sludge compost. A loamy soil was amended with sewage sludge compost at rates of 0, 5, 10, 25 and 50% (v/v). Addition of sludge caused a slight increase in soil pH, and significant increases in electrical conductivity and soluble K, Ca, Mg, NH_4–N and phosphate contents. DTPA–extractable Cu and Zn increased significantly increase was only observed in the treatment with the highest rate of compost application for Cd, Pb and Ni. The yield of Chinese cabbage increased with compost amendment as compared with the control, the highest yield being obtained at the 5–10% application rate. An accumulation of Cu, Cd, Zn, Ni and Pb was observed with an increase in compost application rate. The Cu and Zn concentrations of shoots at the _5% compost amendment rates exceeded the toxic limits of 10 and 20 mg/kg, respectively. Among the metals studied, only Cd resulted in a tissue content higher than the maximum permitted concentration of trace elements in vegetables, at a compost amendments rate of 10%. The results indicate that there should be tight control over the use of the sludge compost for edible crop population.

Nyamangara and Mzezewa (1999) a study was conducted to determine the concentration of EDTA– extractable Zn, Cu, Ni and Pb in a Gleyic Lixisol that had been amended with sewage sludge for more than nineteen years in Zimbabwe. Soil profiles were dug and samples taken for metal analysis using inductively

– coupled plasma atomic emission spectrophotometry (ICP–AES). Sewage sludge addition resulted in a significant ($P < 0.01$) increase in the concentration of the four metals in the top soil (0–15 cm), and there was a significant treatment × soil depth interaction. Zinc decreased from 196 mg/kg in the topsoil (0–5 cm) to 5 mg/kg, in the 15–20 cm horizon while Cu, Ni and Pb decreased form 43 to 11, 23 to 9 and 53 to 19 mg/kg, respectively. The high EDTA–extractable metal concentration in the sludge treatment was due to the spreading of sewage sludge slurry treatment was due to the spreading of sewage sludge treatment was due to the spreading of sewage sludge slurry on the soil, and the accumulation of the metals in the topsoil may be due to the interaction of the metals with organic matter.

According to Elsokkary and Abdel–Salam (1998) field experiments were conducted in Bangar El–Sokkar, Egypt to investigate bioavailability of Cd, Cu, Mn, Ni, Pb and Zn from calcareous soil receiving successive applications of sewage sludge. The field plots were distributed as a randomized complete block with five low sludge rates 0, 5, 10, 15 and 20 t feddan–1 [1 sludge rates of 0, 10, 20, 30 and 40 t feedan–1 [1 feedan = 0.42 hec.] in the first winter growing season (Nov. 95) and in the second winter growing season (Nov. 96). Wheat and faba bean (Vicia Faba) were cultivated in this study. The results showed insignificant effects of sludge applications in the first winter growing season on both DTPA–extractable metals from

soils, metals concentrations in plants and the aboveground biomass yield of faba bean and wheat. By the second winter growing season, the soil had received three successive application rates were increased to 0, 10, 20, 30 and 40 t feedan-1 in the summer season of June 96 and the third application rates were the same as the second. Thus, cumulative amounts of 0, 25, 50, 75 and 100 t sludge feddan-1 were added to the soil. The data of faba bean and wheat soils indicated significant increase in both DTPA-extractable metals, and concentrations of metals in leaves of the two plant species. The harvested aboveground biomass yields (straw and grains) were also significantly increased. The Cd and Zn concentrations in the leaves of the crops and also that extracted by DTPA from soils were significantly higher than those of Cr and Pb.

Obarska-Pempkowiak et al. (1997) stated that the distribution of nutrients and heavy metals was measured in a constructed wetland system designed for processing domestic sewage (150 person equivalent). The system consisted of a reed root zone filter of the vegetation submergent had (VSB) type with horizontal flow of sewage, and a combination of ditches and soil filters. The facility was situated on the slope of a hill. Sewage was pretreated in a Imhoff tank and a trickling filter. Nitrogen, phosphorus and a number of heavy metals, including Mn, Cu, Zn, Cd, Pb, Cr were measured in the various components of the constructed wetland system from 1995 to

1997. Nutrients were removed mostly in the VSB filter section and in the first dam of the cascade filter. Sediments found in ditches after several years of operation consisted of plant debris. In the first ditch the depth of sediments was 5–8 cm, while in the last one its was only 2–3 cm. The heavy metal contents of suspended matter decreased along the course of treatment, starting from the VSB filter, through the first ditch to the last ditch. The main mechanism for removal of dissolved metals was sorption on particulate matter suspended in subsequent ditches. Manganese concentration was controlled by redox conditions in the various sections of the system, and was substantial in ditches rich in organic matter. Nutrients analyses in reed plant samples indicated that accumulation in biomass played an insignificant role in the distribution of analysed elements in the system.

According to Manko and Terelak (1999) the effect of sewage sludge on the mobility of zinc, cadmium, lead, nickel and copper in metal contaminated soil was studied in a microplot experiment. Heavy metals were analysed using Tessier's sequential extraction. The studies showed that sewage sludge demonstrates a potential for reclamation of chemically degraded soils. Application of sludge to the soil reduced the amounts of heavy metals in readily available forms while the less mobile forms increased. The decrease of metal mobility was associated with metal binding by organic matter and precipitation due to alkalinity related to significant amounts of calcium present in

sludge. The immobilization of metals by sludge was caused by their geochemical properties in the following order: Zn > Pb > Cd > Cu > Ni.

Ansari et al. (1999) suggested that different vegetables grown separately in agricultural soil and soil amended with sludge samples were collected from Mirpurkhas and Hyderabad city, Pakistan, in identical conditions. The edible and non–edible parts of each vegetable were analysed to measure metal ion content and comparative studies for correlation and assimilation of various metals from sludge was accomplished. In developing countries like Pakistan, little attention is focused on pretreatment of urban or industrial waste water sludge samples. Mostly the sludge is directly mixed with agricultural soil as supplement fertilizer. In absence of any pretreatment of sewage sludge to remove any excess of toxic elements from sludge, it is feared that their presence accelerates uncontrolled absorption of metals by various parts of plants and fruits during growth creating a potential health hazard. To investigate this problem, samples of sludge were collected from Mirpurkhas division and various domestic and industrial areas of Hyderabad. The analysis of soil and sludge samples and vegetables for different micronutrients and toxic elements was accomplished using reliable analytical methods. It was observed that the levels of Cu, Cr, Cd, Pb, Ni and Zn were higher in sludge samples of industrial area than the agricultural soil, Mirpurkhas and

domestic areas of Hyderabad. The level of the elements was high in vegetables grown in soil amended with industrial sludge.

El-Gendi et al. (1999) reported that surface soil samples (0–20 cm) were taken from two sites in Giza Governorate, Egypt, to determine the forms of selected metals in the solid phases. The first site was irrigated with sewage water effluent for 7 year period, while the second site was for reference. Maize was grown on the soils. The selected soil samples were analysed for total Cd, Pb, Ni and Co contents. These metal were sequentially extracted into operationally defined geochemical fractions; exchangeble, bound to carbonate, bound to Fe–Mn oxides, bound to organic matter, and residual forms. The soil irrigated with sewage effluent showed elevated total contents of the tested metals; Pb (147.4) > Cd (85.87) > Ni (37.38) and Co (10.97 μg/g). On average, metal recoveries were less than the total independently determined total metals content by 9%. In uncontaminated soil, the highest amount of Cd and Pb (35%) was associated with Fe and Mn oxides fraction; while the organically bound fraction, while the organically bound fraction was the dominant form of Co (65%) and of Ni (35%). In sewage water effluent-treated soil, the organically bound fraction was the dominant form throughout the tested metals, accounting for 31, 39, 43, 55% of the Ni, Cd, Co and Pb, respectively. Maize grown to maturity in the selected soils was sampled. In the foliage, Ni (10.8 μg/g) showed the highest concentration among the tested

metals followed in decreasing order by Pb, Co and Cd. The tested metals may have the ability to remobilize in were 26, 23, 10 and 1.5 times greater than the typical for uncontaminated soil.

Tsadilas et al. (1999) conducted a field experiment with cotton was conducted on a well drained, calcareous clay loam (Typic Xerochrept) in Greece to investigate the use of sewage sludge as a partial substitute for fertilizers and the influence of its application on the basic soil properties and heavy metal concentrations. Soil pH was reduced in the case of higher sewage sludge rate. Electrical conductivity, organic matter content, total N, and available P were significantly increased. Total concentrations of Zn, Pb and Cu were slightly increased. DTPA-extractable Zn, Cu and Mn were also significantly increased.

Groenenberg et al. (1999) investigated the chemical forms and biological availability of pollutants; to investigate the effects of acidification on the mobility and toxicity of pollutants; to investigate accumulation of metals in forest litter; and to investigate the effects of water saturation on the mobility of arsenic. Current availability of Cr and As was low, while that of Zn, Cd and Cu was high on heavy polluted sites. Soil acidification increased the availability and ecotoxicity of Cr, Cd and Zn. It is concluded that afforestation will increase soil acidification and the availability of Cr and heavy metals, and additional measures to compensate soil acidification (e.g. liming) are recommended.

Samaras et al. (1998) studied the influence of sewage sludge application on the total and available forms of Zn, Mn, Cu, Fe, Pb, Cd and Ni in a 2-year field experiment in Greece. After 2 years of sewage sludge application, soil samples were taken from all the plots from a depth 0 to 50 cm and the concentrations of the total and available forms (DTPA extractable) of the above mentioned heavy metals were determined. The results showed that sewage sludge application significantly increased the total concentration of Cu, Zn and Pb in the surface layer. Total concentration of Cu, Zn and Cd were strongly correlated with organic matter content. DTPA extractable Cu, Zn, Cd and Fe were also strongly correlated with organic matter content positively and negatively with soil pH.

Martinez and Motto (2000) monitored total dissolved concentrations of Pb, Zn and Cu in seven metal–amended soils (a calcareous and six acid mineral soils). As expected, solubility of added Pb, Zn and Cu increased with a decrease in pH. Furthermore, the results showed that the solubility relationship with pH was similar in all non–calcareous soils. This suggests that metal solubility may be controlled by similar soil components, presumably involving soil components, presumably involving soil characteristics such as pH, organic matter content and soil mineralogy.

Khaled and Sewailem (1999) conducted distribution of Fe, Mn, Zn and Cu in sandy soil amended with sewage sludge. Two

rates (3 and 6%) of sewage sludge were applied to the surface of soil columns. Both doses of sludge added to soil resulted in a marked increase in the total amount of studied micronutrients. Maximum concentrations of metals were found in the surface 5 cm of the soil at a sludge rate of 6% where Fe > Mn > Zn > Cu. Most movement and amount of metals recovered from soil were predominantly limited to a depth of 15, 20 and 25 cm for Fe and Mn, Zn and Cu respectively.

Fang and Wong (1999), studied a batch composting to evaluate the feasibility of co–composting sewage sludge with lime, aiming at reducing the availability of heavy metals in the sludge compost. Liming raised pH of compost effectively at the initial stage of composting and caused a decrease in EC through precipitation of soluble ions. Lime amendment also significantly reduced water–soluble and diethylene triamine pentacetic acid (DTPA)–extractable metal contents. The maximum reductions were 60 and 40% for Cu, 80 and 40% for Mn, 55 and 10% for Zn, and 20 and 25% for Ni at the end of the composting period for the lime–amended sludge as compared to the control. A lime amendment of 1.0% is recommended to co–compost with sewage sludge.

Giri and Bhattacharyya (1999) investigated the solid waste generated in Wazirpur industrial area of Delhi, India. Twenty–four representative samples were collected from three different blocks for the analysis of 12 physicochemical parameters to

characterize these solid wastes. The results showed that the generated wastes were acidic (pH 3.48) with an electrical conductivity of 75 mS/cm, moisture content 35.67%, water holding capacity 52.85%, organic carbon 2.518%, available N 216 ppm, total N 0.292%, available P 42 ppm, total P 0.182%, and C:N ratio 9.33. The total concentration of nutrient elements were K 0.230%, Mg 0.420%, Ca 1.900%, Na 1.510%, Fe 12.300%, Zn 0.040%, Cu 0.210% and Mn 1.15%. The total concentration of toxic metals were Cr 9643 ppm, Cd 83 ppm and Pb 100 ppm. Lime treatment would be required before the wastes could be used for agriculture.

Baveye et al. (1999) reported that total soil concentrations of Cd, Cr, Cu, Ni, Pb and Zn had been significantly enhanced by all sludge application rates to a soil depth of 30 cm. Below the 30 cm depth, total soil Cd was increased to 75 cm, total Zn to 45 cm (T2 and T3 only), total Cr to 60 cm (T2 and T3 only), but total Cu, Pb and Ni were not increased at depth.

Ramachandran and D' Souza (1998) reported that in an Ultisol the acidic soil conditions and low cation exchange capacity values produced a large Cd accumulation and inhibited dry matter yield. DTPA extractable levels of Cd, Zn and Mn in soil after harvest indicated a significant increase in plant available Cd and Zn in the Vertisol and a significant decrease of Mn in the Ultisol.

Peter et al. (1998) reported that concentrations of Cd in

leaves and roots and concentrations of Pb and Zn in roots of Ambrosia trifida were significantly lower in plants collected from limed thàn from unlimed sludge–treated subplots. Liming significantly reduced concentrations of Cd in leaves and roots of solidago Canadensis and in the leaves, roots and seeds of sitaria faberi to levels found in untreated reference subplots. Liming also significantly reduced concentration of Cu in the roots of Solidago Canadensis, Pb in the roots and seeds of Setaria faberi and Zn in the roots and leaves of S. faberi to reference levels.

Sanchez et al. (1997) studied Fe, Cd, Cu, Ni, Pb, Zn and Mn which are frequently present at low concentrations in sewage effluent used for crop irrigation in Mexico. The dry weight of P. Vulgaris decreased significantly with increasing concentration of heavy metals in the external solution. Fe, Mn, Zn, Cd and Ni concentrations in the leaves, stems and roots were directly proportional to the external concentration. At harvesting, roots contained the greatest accumulation of heavy metals in all treatments. Following significant heavy metal uptake, heavy metal ions were transported to the flowers and/or seeds, and this is discussed in relation to human health.

Hamon et al. (1999) reported that radish (Raphanus sativus) was grown in a soil historically amended with sewage sludge at different rates and concentrations of Cd and Zn in the plants and in corresponding rhizosphere soil solution were examined. Metal concentrations in the plants displayed a plateau

response. However, concentrations of total or free metals in the soil solution did not display a similar plateau response, therefore the pre-requisite for determining that metal uptake by plants was limited by sludge chemistry was not met. It was concluded that plant physiological factors were responsible for the plateau in plant metal concentrations observed in this study. Examination of data by other authors suggests that a plateau response due to plant physiological factors has routinely been misinterpreted as being the result of only attenuation by sludge chemistry. The serious implications of an incorrect interpretation of the factors underlying a plateau response are discussed.

Ibekwe et al. (1995) reported that effects of sludge-borne heavy metals on plant growth, nodulation, and nitrogen (N_2) fixation of lucerne (Medicago sativa), white clover (Trifolium repens), and red clover (Trifolium pretense) were examined. Plants were grown in the greenhouse in pots containing a fine sandy loam soil (Typic Paleudults) obtained from plots where heat-treated and Nu-Earth sludges were applied in 1976 and 1978, respectively. Two soil pH regimes (low and high) were examined for each of the treatments. Nitrogen fertilizer (NH_4NO_3) was applied to one-half the pots and each legume was inoculated with the appropriate Rhizobium culture. Soil pH and sludge type significantly affected uptake of metals with phytotoxicity observed in the Nu-Earth, low pH soil. Nodulation was reduced, but not always completely eliminated in all low pH

treatments, including the controls. Symbioses were generally ineffective in low pH treatments. In soils where pH was above 6.0, there was a significant increase in shoot weight and total shoot N with sludge addition. Plants derived significant quantities of N from the soil, where sludge was applied many years ago. When pH was maintained at 6.0 or higher the results show that heavy metals in soils, and the resulting concentration in plants, had no effect on any of the parameters examined.

According to Misra & Mani (1994) the effects of sewage sludge (0, 15, 20 or 25 t/ha) and Mussoorie rock phosphate (MRP; 0, 125, 150 or 175 kg P_2O_5/ha) on the growth and yield of spinach, fenugreek and lettuce were investigated. No harmful effects on growth were observed following sewage sludge treatments. The content of heavy metals in plants, particularly Zn, increased at increasing rates of sewage sludge. In combined Cr and Pb decreased with increasing rate of MRP. No treatment decreased the concentration of Zn in plant tissues to control concentrations.

According to Witter (1996) the Swedish Environmental Protection Board aims to decrease the metal load of soils until a situation of zero accumulation is reached. With the possible exception for Cd, there is no evidence to suggest that zero accumulation of metals in soil is required to protect soil productivity, the environment and human and animal health. A policy of zero accumulation may therefore seem excessively

cautious. However, the policy also recognises the practically irreversible nature of elevated heavy metal concentrations and their effects in soil, the deficiencies in the evidence currently available with which to establish safe metal loadings for soils, as well as the need to preserve the agronomic value of soils. It is argued that the use of restrictive annual metal loading rates can be used to effectively ensure that maximum soil concentrations or cumulative pollutant loading, considered to be safe are not reached in the future.

Hani (1996) reported that the field trials show that increased nutrients (mainly P) and heavy metals in soil due to agricultural use of sewage sludge have mainly to be expected when sludge is applied in too high amounts. The biological effects of heavy metals on plants are determined by their solubility which is increased by pH decrease and degradation of organic matter. Normally, it should be expected that the microbial activity in soil would increase with the application of organic matter in sewage sludge. But, there are also negative effects on the microflora by simultaneous enrichment of organic matter or inorganic and organic pollutants. The main deleterious effects on soil microorganisms are the reduction in size of the total biomass, a reduced nitrogen fixing activity and changes in the composition of microbial populations of the soil. At what stage heavy metal toxicity to soil microorganisms or to microbial processes in soil is likely to become evident is still uncertain.

The soluble fraction of heavy metals (also of organic pollutants) is a determining factor. To minimize the shown environmental risks an adequate sludge management is proposed.

Mortvedt (1996) study of the commercial phosphate (P) fertilizers contain small amounts of heavy metal contaminants which were minor constituents in phosphate rock (PR). Animal manures and sewage sludges (biosolids) are the main organic fertilizers and the latter also may contain heavy–metal contaminants. Heavy metals in biosolids may be found in the inorganic form or may be organically complexed, which could affect their chemical reactions in soil. These heavy metals may accumulate in soil with repeated fertilizer applications. Cadmium (Cd) is the heavy metal of most concern because it may affect human health. Other heavy metals of possible significance are arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), and vanadium (V). Some countries have set tolerance limits on heavy metal additions to soil because their long–term effects are unknown. These limits usually are set for the tillage layer (surface 20–30 cm) of soil where most root activity occurs. Controls on heavy metals concentrations in sewage biosolids and their max. Total and annual loading rates to soil have been imposed in some countries. Regulations also have been proposed for phased in limits on max. heavy metals concentration permitted in P fertilizers, or they are already in affect. Most of the fertilizers relate, Cd limits to a P concentration, so P

application rates indicate Cd inputs to soil. Regulations affecting sewage biosolids include a number of heavy metals, while those concerning P fertilizers only currently include limits on Cd.

Warman et al. (1995) study to assist in the formation of appropriate compost standards in Canada a research project was undertaken in October, 1993 to determine the bioavailability of metals (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn) from compost and compos metal mixtures. Swiss chard (Beta vulgaris) was grown in compost amended soil (Loamy sand soil) comprising 0, 25, 50, 75 or 100% v/v compost (race–track manure–biosolids compost supplemented with a high metal biosolids). Dry matter yield, metal content of tissues, and total metal uptake by plants were determined alongside total (HNO_3) and DTPA–extractable metal content of the compost–soil mixes. The DTPA–extractable and total metal contents were highly correlated; however, neither was correlated with plant metal concn or metal uptake. Further research into the correlation between metal bioavailability and chemical extraction methods was recommended.

Yamamoto and Watanabe (1996) of the experiments to determine the behaviour of heavy metals in sewage sludge applied to the soil surface. The results showed: (1) domestic sewage sludge contained 0.25–0.30 kg/kg of organic matter as total carbon. The average Cd content was 3.4 mg/kg, and Cu and Zn were > 1000 mg/kg; (2) the solubility of heavy metals in the

sewage sludge in acid solution was in the order Zn > Pb > Cd > Cu, and 65% of total Zn was the acid–soluble form. The water solubility of heavy metals was in the order Cd > Zn > Pb = Cu. Cadmium was the most soluble element among the four elements, and more than 5% of total Cd was dissolved; (3) the proportion of the acid–soluble fraction of the metals increased with the decomposition of organic matter in the sewage sludge; (4) the acid–soluble amount of heavy metals in the soils was in the order Cd > Pb > Zn = Cu. Acid soluble Zn was less than 10% of total Zn, indicating that the form of Zn in the soil was different from that of the sewage sludge; (5) the vertical distribution survey of heavy metals in the soil profile indicated that dissolved heavy metals from sewage sludge were not adsorbed in the sandy layer but were adsorbed and accumulated in the clay layer; and (6) 85% of the organic matter in the sewage sludge applied to the soil surface disappeared in 75 days, and 50% of Pb, 70% of Cu, and 70–95% of Zn and Cd disappeared during same period.

The effects of sewage sludge and coal shale on the accumulation of the mobile forms of Pb, Ni, Cd and Cr in dernopodzolic soils of the Perm region of Russia were studied by Krasnaiak (1994). Sewage sludge utilization resulted in a two–to–three–fold increase in concentration of pollutants in the topsoil as compared with the control. Coal shale, which possesses great sorbability, markedly reduced the mobility of heavy metals. Shale can thus be used as an amendment in soil

detoxification.

Wong and Cheung (1995) studied the effects of increasing loading of heavy metals on the anaerobic digestion of sewage sludge. Sludge from Taipo Sewage Treatment Plant, Hong Kong, had a higher gas yield than sludge from Shatin Sewage Treatment plant, due to the higher heavy metal content, including Cr, Cu, Ni and Zn, in Shatin sludge. Adding pig manure to both sludge raised their biogas yields. Dosing concn of the four metals to Taipo sludge showed that gas yields were severely inhibited at the highest concn of each metal tested was in the order of Cr > Ni > Cu > Zn. Microalga, Chlorella pyrenoidosa, was cultivated on water extracts of the digested materials. 5% extracts of both sludges alone gave higher algal growth than the control (Bristol's medium). Extracts obtained from the digested materials containing pig manure gave poorer algal growth.

Electrometric studies of the interaction of heavy metal ion such as manganese, chromium, nickel, copper, zinc, cadmium and lead with humic and fulvic acids from the sludge in a sewage oxidation pond were conducted Wasay et al. (1993). Most metal ions (up to 97%) were bound by humic and fulvic acids. Sludge containing metals was burnt at 500°C to obtain ash, from which the metals were leached with nitric acid. The efficiency of metal removal on sludge ash was greater than 97%.

Chapter III

MATERIALS AND METHODS

Chapter – III

MATERIALS AND METHODS

The present study on "Studies on the metallic Pollution in soil" was conducted during the years 2000, 2001 and 2002. The details of materials and methods employed are as follows:

LOCATION OF THE EXPERIMENTS:

The site for most of the experiments was Experimental Farm of Sheila Dhar Institute of Soil Science (SDI) which is situated at Mumfordganj. Two sides of the farm are surrounded by the municipal drains. The whole farm is being irrigated by municipal sewage water for more than one and half decade. Mostly seasonal vegetables are grown on this farm. Some portion of the S.D.I. farm is low lying area. This low lying area was subjected to dumping of municipal waste.

The discharge of thirteen big drains carrying sewage sludge from different parts of the city find their way directly into the rivers Ganga and Yamuna. At present about 40 million liters of sewage sludge flows down into these rivers without being treated.

For the study of quality of sewage water for irrigation and heavy metal contents in sewage sludge, samples were collected from different places and analysed.

CLIMATE:

Winters at Allahabad are very cold and summers intolerable. Total annual rain fall in this district is 83.0cm and average annual temperature

varies from 32.4°C to 37.5°C. The humidity is about 64%.

SOIL:

The soil of Sheila Dhar Institute research farm is alluvial (Entisols), having a good water holding capacity and medium organic carbon content. The texture of soil is sandy clay loam.

FIELD EXPERIMENT:

The field experiments laid out at Sheila Dhar Institute experimental farm in randomized block design (R.B.D.) having seven treatments and three replications. The size of the microplots was kept $1m^2$.

FIELD PREPARATION:

The soil of the plots was worked with the help of spade, then it was irrigated with tap water. After four days the blocks and plots were prepared for treatment and sowing of crops.

METHOD OF COLLECTING SEWEAGE SAMPLES:

Composite individual samples were collected in one litre polythene bottle from different selected places and all such samples were thoroughly mixed to get representative sample for analysis of metals and soluble salts. One litre of such representatives sample is sufficient for all determinations. The sampled bottles were tightly stoppered to prevent any CO_2 being absorbed from the atmosphere to decrease the pH value of the samples.

PRESERVATION OF SAMPLES:

In glass sample containers, some of the elements like Cd, Cr, Cu, Fe,

Mn and Zn may be absorbed on walls of the containers. Such losses due to absorption are higher particularly at a pH around '7'. However, by lowering the pH of water samples to 2 or less by HNO_3, the losses can be reduced considerably.

In the present study, sewage water was analysed for heavy metals, like Cd, Cr, Cu, Fe, Mn, Pb and Zn. The sewage samples were collected in polythene bottles and pH below 2.0 was adjusted by the addition of 5ml, conc. HNO_3.

METHOD FOR HEAVY METALS DETECTION IN SEWAGE:

Metals have the tendency to form complexes readily with the organic constituents, hence it is necessary to destroy them by digestion with strong acids. This preliminary acid digestion not only destroys organic matter but also brings all suspended metallic compounds into the solution.

DIGESTION WITH NITRIC ACID:

For the estimation of Cd, Cr, Cu, Fe, Mn, Pb and Zn, nitric acid digestion was adopted. 100ml sample was taken in a 250ml beaker and 5ml conc. HNO_3 was added. The mixture was brought to a slow boil and then evaporated on a hot plate to the lowest volume (15–20ml). To the remaining portion 5ml conc. HNO_3 was again added and the contents heated to a gentle refluxing action. The contents were cooled and walls of the beaker were washed down and then contents filtered. The filtration was taken in a 100ml volumetric flask and mixed thoroughly.

ANALYSIS OF METALS:

20ml digested solution was taken for each metal to be detected with the help of PYE UNICAM SP 2900 coupled with SP–9 computer Atomic Absorption Spectrophotometer using Standard methods (1976).

ANALYSIS OF SOIL FOR HEAVY METALS:

In order to find out the total contents of heavy metals, a di–acid mixture was used. To 1g of soil, 5ml conc. HNO_3 and 5ml of $HClO_4$ (60%) were added and the contents were heated up to dryness. Then hot distilled water was added, the contents filtered and volume was made up to 50ml.

The heavy metals were detected with the help of the Atomic Absorption Spectrophotometer (AAS).

PREPARATION OF DTPA SOLUTION:

DTPA solution was used to extract the available heavy metals in soil samples.

1.97g (0.05M) DTPA power, 13.3ml (0.1M) Tri–ethanol amine and 1.47g (0.01M) Calcium chloride were dissolved in distilled water and the volume was made up to 1 litre after adjusting the pH to 7.3.

EXTRACTION OF SOIL BY WITH DTPA SOLUTION:

To 10g soil 20ml DTPA solution was added and the contents were shaken for two hours and then filtered through filter paper No. 42. This extract was utilised for the determination of available heavy metals by AAS.

EXTRACTION OF SOIL BY WITH HCl SOLUTION:

The HCl extract was obtained by heating a mixture of 5g of soil with 35ml of 1N HCl overnight in a Tyler tube at 70°C. Then 15ml of water was added and the resulting mixture was allowed to settle. The supernatant liquid was filtered and analysed for metals.

EXTRACTION OF SOIL BY WITH TRI–ACID SOLUTION:

The tri–acid extract was obtained by heating a mixture of 5g of soil with 35ml tri–acid mixture ($10HNO_3$: $4HClO_4$: $1H_2SO_4$) overnight in a Tyler tube at 70°C. Then 15ml of water was added and the resulting mixture was allowed to settle. The supernatant was filtered and analysed for metals.

METHODS OF SOIL ANALYSIS:

Collected soil samples from the Sheila Dhar experimental farm as well as from other sewage–sludge irrigated areas were analysed by standard methods given by Jackson (1967).

SOIL pH:

Soil pH was measured using ELICO pH meter at 1:2.5 soil water ratio.

ORGANIC CARBON:

Organic carbon was determined by rapid titration method of Walkley and Black and the values were converted to organic matter by multiplying with Bemmlen factor, i.e. 1.724.

CALCIUM AND MAGNESIUM:

Ca and Mg were determined by EDTA method.

CATION EXCHANGE CAPACITY:

Cation exchange capacity was determined by using neutral normal ammonium acetate solution.

PHOSPHATE:

P was determined by Olsen's method (0.5M. $NaHCO_3$ pH 8.5) with the help of colorimeter.

NITROGEN:

Total nitrogen was estimated using Kjeldahl digestion method.

POTASH:

K was estimated by Flame photometer method.

METHOD FOR PLANT ANALYSIS:

Plant samples viz. Spinach (Spinach oleracia L.), Fenugreek (Trigonella foenumagracecum) and Radish (Raphanus sativus) were collected along with roots, washed with de-ionized water and then dried in an oven. Dried plant material was ground and digested is acids for metal analysis.

DIGESTION OF PLANT MATERIALS:

2.0g of ground plant material was taken in a 100ml beaker and 20ml

of an acid mixture (750ml of conc. HNO_3, 150ml of conc. H_2SO_4 and 300ml of $HClO_4$) was added. The contents were heated on a hot plate at low heat for 30 minutes and the volume was reduced to about 5ml. After cooling, 20ml distilled water was added to the beaker and the contents filtered through filter paper No.1 into a 100ml volumetric flask and the volume was made up with distilled water.

Heavy metals in plants were determined directly using Atomic Absorption Spectrophotometer.

PRINCIPLE UNDERLYING AAS:

When an atom, ion or molecule absorbs a photon, the added energy results in a transition alteration of sate; the species is then said to be excited. Excitation may involve any of the following processes:

- Transition of an electron to a higher energy level.
- A change in the mode of vibration of the molecule.
- Alteration in its mode of rotation.

Each of these transitions require a definite quantity of energy, the probability of occurrence for a particular transition is greatest when the absorbed photon supplier precisely this quality of energy.

The energy requirements for these transitions vary considerably. In general, promotion of electrons to higher levels requires greater energies than those needed to bring about vibrational changes. Alterations in rotational modes are likely to have the lowest energy requirements of all. Thus, absorption observed in the microwave and far infrared regions will be

due to the shift in rotational level since the energy of the radiation is sufficient to cause other types of transitions. Changes in vibrational levels are responsible for absorption in the near infrared and visible regions. Absorption due to promotion of an electron to some higher energy level takes place in the visible, ultraviolet and x–rays regions of the spectrum.

In spectrophotometric analysis, light of definite wave–length, say 1–10Å bandwidth, extending to the ultraviolet region of the spectrum constitutes the sources of light.

When a beam of radiant energy falls upon a substance, the energy of the beam is partly altered by reflection, refraction, diffraction or absorption and the remainder of the energy may be transmitted through the substance.

If I_0 = Thc intensity or amount of energy per square centrimeter per second before passing through the substance.

I = Intensity of energy after passing through the solution.

Then, the fraction of the light transmitted is called transmittance(T)

$$T = \frac{I}{I_0}$$

Absorbancc (A) is dcfined as $A = \text{Log}_{10} = \frac{I_0}{I}$

It is also called optical density. Accordingly the relation between the two is

$$A = \text{Log}_{10} = \frac{I}{T}$$

Table 3.1

Physico–chemical properties of sewage irrigated soil of Sheila Dhar Institute (SDI) experimental farm, Allahabad (2000).

pH	7.4
EC (D Sm^{-1}) at 25°C	0.18
Organic Carbon	0.99%
Total Nitrogen	0.08%
C.E.C. [C $mol(p^{+})kg^{-1}$]	19.8
Total Phosphate	0.09%
DTPA Cd	0.48 ppm
DTPA Cr	0.34 ppm
DTPA Cu	0.36 ppm
DTPA Pb	0.34 ppm
DTPA Zn	4.80 ppm
DTPA Fe	13.50 ppm
DTPA Mn	12.60 ppm

Table 3.2

Physico–chemical properties of sewage water available at S.D.I. experimental farm in the year 2000.

PH	7.4	–	7.7
EC (dsm^{-1}) at 25°C	845	–	1930
Total Solids (mg/l)	190	–	435
Total hardness (mg/l)	182	–	225
Alkalinity (mg/l)	132	–	242
Chloride (mg/l)	15.0	–	32.0
Total Nitrogen (mg/l)	0.03	–	0.076
Phosphate (mg/l)	0.06	–	1.5
Sulphate (mg/l)	4.60	–	12.0

STATISTICAL ANALYSIS:

Statistical analysis was done with the help of Sum of Square (S.S.) and Degree of Freedom (D.F.).

The method of analyzing the data has been illustrated in the following way:

(i) Tabulation: The observed data were tabulated according to treatments and replications.

(ii) S.S. for different sources of error.

(a) Correction factor (C.F.) = $\sum \frac{Rt^2}{nk}$

Where, $\sum Rt$ = Total of all the variates/replications.

n = Number of variates/replications.

k = Number of lots/treatments.

(b) Total S.S. = $\left(X_1^2 + X_2^2 + X_3^2 + ... + X_{kn}^2\right)$ – C.F.

Where, X_1, X_2, X_3 .... X_{kn} are variates/data.

(c) S.S. due to variates/replications $= \dfrac{T_1^2 + T_2^2 + ... T_n^2}{k}$ – C.F.

Where, T_1, T_2 ..... T_n are total of different lots/treatments

(d) S.S. due to lots/treatments = $\dfrac{Rt_1^2 + R_2^2 + ... Rt_k^2}{n}$ – C.F.

Where, Rt_1, Rt_2 ... Rt_k are total of different variates/replications.

(e) S.S. due to error=(Total S.S.)–(S.S. due to variates/replications)

–(S.S. due to lots/replications)

(f) M.S. due to lots/treatments $= \dfrac{\text{S.S. due to lots / treatments}}{(k-1)}$

(g) M.S. due to error $= \dfrac{\text{S.S. due to error}}{(n-1)\ (k-1)}$

(h) Variance ratio $= \dfrac{\text{M.S. due to lots / treatments}}{\text{M.S. due to error}}$

(iii) Standard Error (S.E.) $= \sqrt{\dfrac{2V_E}{n}}$

Where, V_E = Variance due to error

& n = number of replications

(iv) Critical Difference (C.D.) = $S.E_{diff} \times t_{5\%}$ ($t_{5\%} = 2.179$)

The observed value of F was compared from the tabulated F –value at 5% and 1% level of significance.

PEARSON'S COEFFICIENT OF CORRELATION:

This measure of correlation obtained by *Prof. Karl Pearson* is based on the arithmetical descriptions. It is usually denoted by the symbol 'r'. This measure is quite capable of expressing the direction and the exact amount of casual relationship between the two variables under study. It has been seen that the values of 'r' always lie between–1 and +1. Further we note that for a value r = +1, there is perfect (+)ve correlation; for r= –1, there is perfect (–)ve correlation; and for r=0, there is no correlation between the two variables. Also for a value of r lying between 0 and 1, there is limited (+)ve correlation between the two variables. If we consider a random sample of n pairs in (x,y) drawn from a bivariate normal population, then Pearson's coefficient of correlation or the product moment coefficient of correlation is given by the formula–

$r = \frac{c_0v(x,y)}{\sigma_x \ \sigma_y}$, where cov (x,y) = $\sum(x-\bar{x})y-\bar{y})/n$ stands for the sample–covariance of x and y, $\sigma_x = \sqrt{[\Sigma(x-\bar{x})^2/n]}$ and $\sigma_y = \sqrt{[\Sigma(y-\bar{y})^2/n]}$ stand for sample–s.ds. of x and y respectively. Thus by using the direct method, we have

$$r = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{\sqrt{[\Sigma(x-\bar{x})^2 \Sigma(y-\bar{y})^2]}}$$

Testing the significance of an observed correlation coefficient r when ρ=0. Let r be the correlation coefficient of a random sample of n pairs drawn from a bivariate normal population with zero correlation coefficient. Then testing the significance of the observed r is the same as testing the significance of difference (r–0), or ρ=0. Here we usually test the hypothesis (H_0)–that the sample has been taken from a bivariate normal population with zero correlation coefficient, i.e. ρ=0. If the hyp. is true, we compute the statistic

$$t = \frac{r}{\sqrt{[(1-r^2)/9n-1)]}}$$ which follows a 't' distribution with (n–2) d f.

Here the quantity $\sqrt{[(1-r^2)/(n-2)]}$ is the s.e. of r in a random sample of n. If the absolute value of this statistic i.e. $|t| \geq t_{05}(n-2)$, we reject the hypothesis at 5% level, otherwise the sample is said to be consistent with the hypothesis.

Chapter IV

RESULT AND DISCUSSION

Chapter IVa

DISTRIBUTION OF HEAVY METALS IN SEWAGE IRRIGATED SOILS

Chapter – IV A

DISTRIBUTION OF HEAVY METALS IN SOIL

Detailed studies regarding the enrichment of heavy metals in soil profile, especially those irrigated with sewage water are lacking. The present study was undertaken with a view to analyse the soils from various sites, receiving sewage irrigation or sludge addition in order to determine heavy metal pollutant. Depth–wise movement of Cd, Cr, Cu, Fe, Mn, Pb and Zn was investigated in sewage irrigated soils.

EXPERIMENTAL:

Representative soil samples were collected from five different sites of Sheila Dhar Institute Experimental Farm respectively. By and large vegetable are grown on these soils. The primary criterion of the selection of site was the distance from disposal site. The five sites designated as S_1, S_2, S_3 S_4 and S_5 were selected according to increasing distance from disposal site the profile samples from each site were taken from depth 0–15, 15–30, 30–40 and 45–60cm. The samples were air dried, processed and passed through a 2mm sieve and analysed for some importance soil characteristics viz. pH, CEC, organic carbon and clay content using standard procedures. The representative soil samples were analysed for seven heavy metals i.e. Cd, Cr, Cu, Pb, Mn and Zn using AAS.

For the available content of these heavy metals, soil samples were extracted with DTPA and for total content, samples were digested in di–acid mixture and directly analysed by Atomic Absorption Spectrophotometer. Detailed methods are given in chapter–III.

Table IVA–1: Site–wise distribution of Total heavy metals (Cd, Pb, Cu, Mn, Fe and Zn) in sewage irrigated soil of S.D.I. experimental farm (mg/kg).

Site	pH	Organic Carbon %	C.E.C. me./100 g soil	Total (mg/kg)					
				Cd	Pb	Cu	Mn	Fe	Zn
S_1 Farm south	7.3	0.60	19.5	2.0	80.0	94.0	450.0	300.0	305.0
S_2 Farm North	7.2	0.77	17.5	2.6	40.0	48.0	405.0	285.0	140.0
S_3 Farm East	7.4	0.70	15.9	1.8	32.0	27.0	315.0	290.0	75.0
S_4 Farm West	7.6	0.92	15.3	1.6	25.0	25.0	265.0	280.0	50.0
Mean	–	–	–	2.0	44.25	48.50	358.75	288.75	142.50
S.E.	–	–	–	2.93	12.24	5.23	7.62	1.57	9.64
C.D.	–	–	–	6.40	26.67	11.40	16.60	3.42	21.00

Table IVA–2: Site–wise distribution of DTPA–Extractable heavy metals (Cd, Pb, Cu, Mn, Fe and Zn) in sewage irrigated soil of S.D.I. Experimental Farm (mg/kg).

Site	pH	Organic Carbon %	C.E.C. me./100 g soil	DTPA extractable (mg/kg)					
				Cd	Pb	Cu	Mn	Fe	Zn
S_1 Farm South	7.3	0.60	19.5	0.20	10.0	15.00	20.00	46	12.5
S_2 Farm North	7.2	0.77	17.5	0.12	6.5	12.00	17.00	44	3.6
S_3 Farm East	7.4	0.70	15.9	0.06	3.0	5.00	12.50	35	4.0
S_4 Farm West	7.6	0.92	15.3	0.04	2.5	2.60	10.00	30	2.5
Mean	–	–	–	0.105	5.5	8.65	14.9	38.75	5.65
S.E.	–	–	–	3.95	8.83	3.06	1.78	2.22	4.47
C.D.	–	–	–	8.62	19.24	6.97	3.88	4.85	9.47

Table IVA–3: Enrichment of Total heavy metals in sewage irrigated soils of S.D.I. experimental farm (mg/kg).

Depth (Cm.)	pH	Organic Carbon %	C.E.C. mg/kg soil	Total (mg/kg)						
				Cd	Cr	Cu	Fe	Mn	Pb	Zn
0–15	7.4	0.58	19.8	2.68	9.64	46.00	838	444	4.84	116
15–30	7.2	0.75	17.5	4.14	3.12	44.80	770	612	4.36	148
30–45	7.5	0.68	15.6	4.10	4.26	28.20	726	562	3.44	126
45–60	7.6	0.90	15.20	1.98	2.42	26.80	542	422	1.92	114
S.E.	–	–	–	3.22	11.32	6.34	6.75	6.74	14.69	1.24
C.D.	–	–	–	7.02	24.67	13.81	14.72	14.68	32.02	2.70

Table IVA–4: Enrichment of DTPA–extractable heavy metals in sewage irrigated soils of S.D.I. experimental farm (mg/kg).

Depth (Cm.)	pH	Organic Carbon %	C.E.C. mg/kg soil	DTPA–extractable (mg/kg)						
				Cd	Cr	Cu	Fe	Mn	Pb	Zn
0–15	7.4	0.58	19.8	0.286	0.148	2.48	53.68	19.08	2.60	2.18
15–30	7.2	0.75	17.5	0.164	0.122	2.82	32.56	14.32	1.72	1.50
30–45	7.5	0.68	15.6	0.146	0.122	2.22	17.64	9.60	1.34	1.30
45–60	7.6	0.90	15.2	0.114	0.102	1.52	13.80	7.46	1.10	1.08
S.E.	–	–	–	3.67	3.46	5.07	13.48	21.81	4.88	0.41
C.D.	–	–	–	8.00	7.54	11.05	29.38	47.53	10.63	0.81

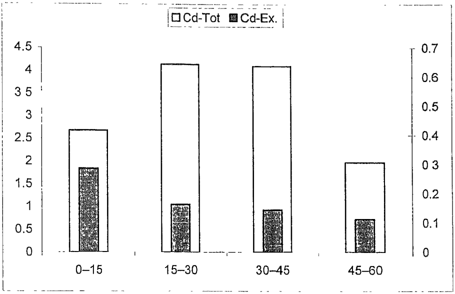


Fig. IVA-1 Distribution of Cd-Total and Cd-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

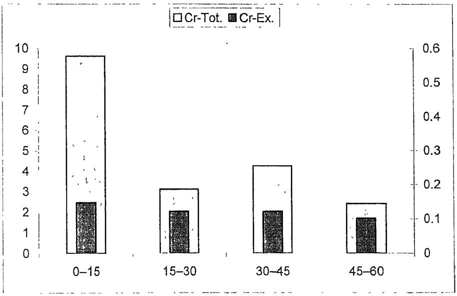


Fig. IVA-2 Distribution of Cr-Total and Cr-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

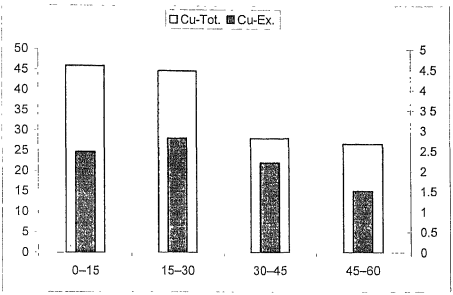


Fig. IVA-3 Distribution of Cu-Total and Cu-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

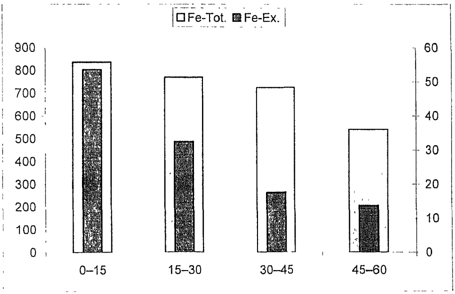


Fig. IVA-4 Distribution of Fe-Total and Fe-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

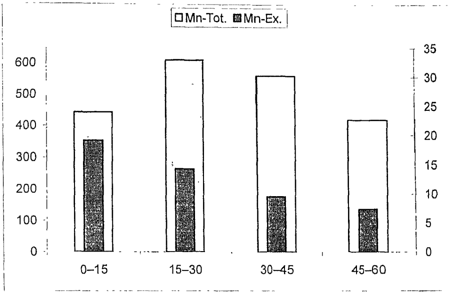


Fig. IVA-5 Distribution of Mn-Total and Mn-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

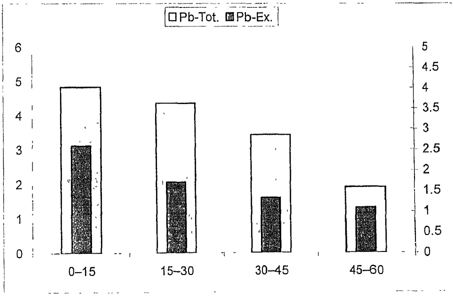


Fig. IVA-6 Distribution of Pb-Total and Pb-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

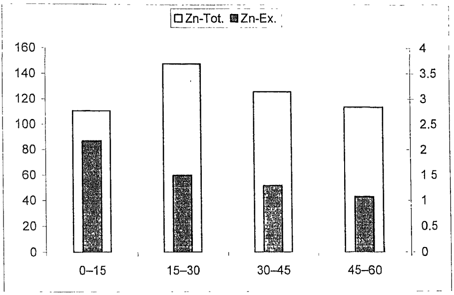


Fig. IVA-7 Distribution of Zn-Total and Zn-Extractable in sewage-irrigated soils (mg/kg) of S. D. I. Experimental Farm

Cadmium (Cd):

It is observed that the sites located within the range 100m from sewage source (S_1 and S_2) got higher conc. of total and extractable Cd content. Total Cadmium ranged from 1.6 mg/kg at site S_4 to 2.6 mg/kg at site S_2, while extractable Cd continuously decreased from 0.20 mg/kg at site S_1 to 0.40 mg/kg at site S_4. (Table IVA – 1 & 2)

The above observation clearly showed that their is gradual decrease in the conc. of Cd from site situated at the sewage canals to the site situated 300m apart from the sewage source. The mean content of total Cd at various sites was observed 2.0 mg/kg, while it was observed 0.105 mg/kg for extractable Cd in S.D.I. experimental farm, Allahabad.

Thus total and extractable Cd varies in sewage irrigated soils at different sites situated apart from the sewage irrigation sources. These results indicate that the nature and quality of sewage water affect the availability of Cd in soil.

The concentration of total Cd did not show any definite trend regarding variation due to sample site or in soil profiles. The total Cd concentration in different soils ranged from 1.4 to 4.6 mg/kg Cd did not show significant correlation with any of the soil properties. (Table IVA –3)

DTPA–erxtactable cadmium also declined with increasing distance from and sewage water application in soils. Average content of DTPA–extractable Cd varied from 0.10 to 0.32 mg/kg. (Table IVA – 4)

The mean content of total Cd at different sites (S_1, S_2, S_3, S_4 and S_5) was observed 3.22 mg/kg. DTPA–extractable Cd was observed maximum

0.80 mg/kg at site S_1 and it was observed minimum 0.67 mg/kg at site S_3. The amount of DTPA–extractable Cd decreases from site S_1 to S_5 as they are situated far away from the discharge point.

Irrespective of the sewage application, the DTPA–extractable Cd content decreases with depth. Mean contents of DTPA–extractable Cd and total Cd in sewage irrigated soils at 0–15, 15–30, 30–45, 45–60cm. depth were found 0.286, 0.164, 0.146 and 0.114 mg/kg and 2.68, 4.14 and 1.98 mg/kg respectively in S.D.I. experimental farm.

The total Cd content in soil profile showed the following trend of their depths 15–30>30–45>0–15>45–60 in their concentration 4.14>4.10> 2.68>1.68 mg/kg respectively. The extractable Cd content observed maximum 0.286 mg/kg of surface layer (0–15) and continuously decreased with the varying depths. It was observed minimum (0.114 mg/kg) at the depth of 45–60cm.

Chromium(Cr):

Total Cr content decreased with depth from 9.64 to 2.42 mg/kg in 0–60cm. depth in sewage irrigated soils. Extractable Cr also decreased with depth in Sheila Dhar Experimental Farm. It decreased from 0.15 to 0.10 mg/kg in the above mentioned experimental farm.

The mean DTPA–extractable Cr decreased from depth 0.148 to site S_4 (0.102 mg/kg) (Table IVA – 4). The mean contents of DTPA–extractable Cr and total Cr in sewage irrigated soils at different depths (0–15, 15–30, 30–45, 45–60 cm.) was found 0.15, 0.12, 0.12 and 0.10 mg/kg and 9.64, 3.12, 4.26 and 2.42 mg/kg respectively.

The depths of soil profile have been compared by setting them in the

descending order of their total and extractable Cr content.

Depth (Cm.)	0–15	15–30	30–45	45–60
Concentration of Total Cr (mg/kg)	9.64	4.26	3.12	2.42
Concentration of Extractable Cr (mg/kg)	0.148	0.112	0.112	0.102

Copper (Cu):

The above observation definitely showed the gradual decrease in conc. of total and extractable Cu from site situated at the sewage source to the site situated apart from it. The mean content of total Cu at various sites was observed 48.5 mg/kg, while it was observed 8.65 mg/kg for extractable Cu in S.D.I. experimental farm, Allahabad. (Table IVA – 1 & 2).

The same result was observed in total and extractable Cu as in the case of total and extractable Cd regarding the variation in conc. at different site. It can be concluded that the nature and quantity of sewage water affect the availability of Cu in soil.

Table IVA 1 & 2 that the mobility of Cu from site to site was observed minimum and it was not significant even at 5% level of significance. It is observed that total and extractable Cu showed definite decreasing trend, in the conc. as the distance from the source of sewage irrigation increases respectively. The conc. of total Cu content ranged from 94 mg/kg at site S_1 to 24 mg/kg at site S_4, while it was observed 15.0 mg/kg at site S_1 to 2.60 mg/kg at site S_4 in distribution of extractable Cu in sewage irrigated soil of S.D.I. experimental farm, Allahabad.

The total concentration of Cu significantly decreased with depth. In almost all the profiles it was irregularly distributed. This type of decrease along the depth indicates the low mobility of Cu down the profile which may be attributed to the formation of cupric humate complex in surface layer having high stability and poor mobility.

The concentration of DTPA–extractable Cu in the soils showed a wide variation in its content due to varying sampling sites and down the soil profile. A gradual decline in its content was recorded with increase in distance from the point of sewage discharge and down the profile of almost all the sites. The data further indicated the enrichment of extractable Cu due to discharge of sewage water and sludge mostly in the surface layer with very little mobility down the profile.

The maximum 46.0 mg/kg total Cu concentration and the minimum 26.8 mg/kg total Cu concentration were observed in the depths 0–15 and 45–60 Cu respectively.

Irrespective of depth mean content of the DTPA–extractable Cu in sewage treated soil of S.D.I. experimental farm at 0–15, 15–30, 30–45 and 45–60 cm. depths was found 2.48, 2.82, 2.22 and 1.52 mg/kg respectively.

The depths of soil profile have been compared by setting them in the descending order as depths of 0–15 > 15–30 > 30–45 > 45–60 cm of their total Cu content as 46.0 > 44.8 > 28.2 > 26.8 mg/kg respectively; while the order of depths was observed as 0–15 > 15–30 > 30–45 > 45–60cm for their corresponding extractable Cr content as 2.82 > 2.48 > 2.22 > 1.52 mg/kg. (Table IVA – 3 & 4).

Iron (Fe):

Table IVA – 1 & 2 shows that the mean content of total and extractable Fe was observed 288.75 mg/kg and 38.75 mg/kg respectively. Same results were obtained regarding the gradual decrease in concentration from site S_1 to site S_4. But the range was observed less in comparison to other heavy metals. Only 6.67% decrease in total Fe was observed from site S_1 to site S_4, while it was observed 34% (decrease in concentration) for DTPA–extractable Fe.

The observations clearly indicate that the mobility of Fe (Fe^{2+} to Fe^{3+}) in sewage irrigation from site to site is very high. Under soil solution the mobility of $Fe(OH)_3$ through sewage–irrigation is dominant, leading to the distribution of total and extractable Fe at various sites. It may be concluded that distance from source of sewage irrigation to destination site is not significant at very high level of significance due to high mobility and solubility of Fe in sewage irrigation.

Total Fe was found to be greatly influenced by varying quantities of sewage sludge application. Though, some profile nearer to the sewage discharge point were rich in Fe in surface samples, rest of the profiles exhibited more or less its uniform distribution along the profile. This uniform distribution of total Fe indicated its high mobility down the profile. The conversion of Fe^{+} into Fe^{3+} during the period of submergence might have facilitated the mobility of Fe down to the surface layer. (Table IVA – 3 & 4).

DTPA–extractable Fe decreased progressively into soil depths. The surface soil sample were sufficiently rich in DTPA–extractable Fe with its maximum concentration at the point of sewage discharge.

The total Fe concentration in different soils, irrigated with sewage water ranged from 500–800 mg/kg. Mean content of total Fe and DTPA–extractable Fe in sewage treated soils of S.D.I. experimental farm at 0–15, 15–30, 30–45, 45–60cm depths were 838, 770, 726, 542 mg/kg and 53.68, 32.56, 17.64 and 13.80 mg/kg, respectively (Table).

Manganese (Mn):

Table IVA – 1 & 2 show that the total Mn content ranged from 265 mg/kg at site S_4 to 450 mg/kg at site S_1. Similarly the DTPA–extractable Mn ranged from 10 mg/kg at site S_4 to 20 mg/kg at site S_1. The decrease in total Mn and DTPA–extractable Mn from site S_1 to site S_4 were observed 41.2% and 50% respectively. The mean content of total and DTPA–extractable Mn were observed 358.75 mg/kg and 14.9 mg/kg respectively.

Highly significant response was observed in the site wise distribution of both total and extractable Mn in sewage irrigated soils. The total and extractable content markedly decreased in the order of respective sites as $S_1>S_2>S_3$ and $>S_4$. Significant amount of Mn, upto 27 mg/kg, were extracted from site S_1 as against only 11 mg/kg at site S_4. It is interesting to note that Mn concentrations were observed second highest after Fe concentration in sewage irrigated soils.

Like other heavy metals with the application of Mn in sewage or other organic waste to agricultural site are subjected to long–term increase

in total soil levels as well the extractable soil levels.

There were marked variation in the total Mn content of soils at different depths but the variation was not regular along the depths at any of the site.

The DTPA–extractable Mn status of the soils at various sites and depths indicates its behaviour similar to others discussed. Higher amont of DTPA–extractable Mn surface and sub–surface depths may be due to the movement of Mn from surface to sub–surface layer of soil profile as these sites are situated nearer to the discharge point of sewge sludge. Sewage sludge treatment seems to be responsible for the accumulation of available Mn in the surface of soil profiles with a tendency of its movement to sub–surface soils.

Table IVA – 3 & 4 show that the total Mn concentration in different soils irrigated with sewage water ranged from 370 to 630 mg/kg. Mean content of total Mn and DTPA–extractable Mn in sewage treated soils of S.D.I. experimental farm at different depths (0–15, 15–30, 30–45, 45–60cm.) were 444, 612, 562 and 462 mg/kg and 19.08, 14.32, 9.6 and 7.46 mg/kg, respectively.

The higher concentration of sub–surface layers (at depths of 15–30 and 30–45cm) to the surface layer verify the mobility of Mn through the soil profile. The concentration of total Mn was observed in various depths as

15–30 > 30–45 > 0–15 > 45–60cm, while extractable Mn was observed in

various depths as 0–15 > 15–30 > 30–45 > 45–60cm in the descending order of their concentration.

Lead (Pb):

It is observed that total content of Pb ranged from 25–80 mg/kg, while it was observed 2.5–10.00 mg/kg for extractable lead. Both total and extractable content of Pb was observed maximum (utmost) at the site of sewage source. About 20–50% decrease was observed as the distance from the sewage source to the destination source increase by 100m. There was marked and gradual decrease observed after each 100m distance of interval from the source to the destination site. (Table IVA – 1 & 2).

Primary considerations with the application of lead (Pb) in sewage or other organic wastes to agricultural soils are long–term increases in total soil levels and changes in metal bioavailability as a result of sewage irrigation or crop management. The average increases in total (sum of fractions) soil Pb for the three soils in this study, from enrichment of the highest rate of sewage–irrigation, were 75, 78 and 87 mg/kg, respectively, while it were observed as 24, 25 and 26 mg/kg, respectively from the enrichment of the lowest rate of sewage irrigation.

Variation in total Pb content along the soil profile from almost all site was negligible. This shows that Pb is preferentially help on the colloidal matrix of the soils forming clay humus complex with the result of negligible downward movement in profile.

The DTPA–extractable Pb different markedly in the surface soil

samples and at varying soil depths. The surface soil sample from the site nearest to sewage discharge point contained appreciably high amount of extractable Pb and gradually decreased as distance from the discharge point increased. The DTPA–extractable Pb was observed to be distinctly higher in surface soil samples them in the sub–surface soils at most of the sites. This shows that mobility of Pb down the profile is very slow or negligible.

Table IVA – 3 & 4 show that the total Pb content decreased with depth from 4.9 to 1.9 mg/kg and DTPA–extractable Pb content decreased with depth from 2.6 to 1.1 mg/kg, respectively. Mean content of DTPA extractable Pb in sewage irrigated soils at different depths were 2.6, 1.72, 1.34 and 1.1 mg/kg.

The depth of soil profile has been compared by setting them in descending order of their total and Pb content.

Depth (Cm.)	**0–15**	**15–30**	**30–45**	**45–60**
Concentration of Total Pb (mg/kg)	4.84	4.36	3.44	1.92
Concentration of Extractable Pb (mg/kg)	2.60	1.72	1.34	1.10

Zinc (Zn):

Table IVA 1 & 2 show that the sites located within the range of 100m from sewage (S_1 and S_2) got higher concentration of total and extractable Zn content. Total Zn ranged from 50mg/kg at site S_4 to 305 mg/kg at site S_2, while extractable Zn ranged from 2.5mg/kg at site S_4 to 12.5 mg/kg at site S_1. Total Zn markedly decreased by 54.1% and

extractable Zn deceased by 71.2%, from site S_1 to site S_2. The decrease was not found significant from site S_2 to site S_3. It was noted that average total Zn content was noted 6.1 times higher and extractable Zn content was noted 5 times higher at site S_1 than at site S_4. It is very interesting that total Zn content was noted 2.14 times higher and extractable Zn was noted 2.21 times higher at site S_1 than their mean contents respectively.

The above findings clearly indicate the low mobility and solubility of zinc in the site–wise distribution in sewage–irrigated soils of S.D.I. experimental farm Allahabad. Increasing the distance from source to the destination site/place reduces the toxicity of heavy metal in relation to Zn concentration.

The sub surface soil samples contained more total Zn that the surface samples except in few sites. Surface soils contained more DTPA–extractable Zn. However, the soil, which was nearest to the discharge point of the sewage sludge, contained appreciably more DTPA–extractable Zn in the surface layer than other sampling sites. There was reduction in DTPA–extractable Zn down the depth in soils receiving sewage sludge continuously but other soils located at distant places from discharge point of sewage water had an irregular trend in variability along the depth. An inverse relationship between pH and extractable Zn has been reported by several workers.

Table IVA – 3 & 4 show that the total Zn content ranged with irrespective of depth from 114 to 148 mg/kg. DTPA–extractable Zn content decreased with depth from 2.18 to 1.08 mg/kg. Mean content of DTPA–extractable Zn in sewage irrigated soils at different depth was 2.18, 1.50,

1.30 and 1.08 mg/kg. The descending order of various depths as 15–30 > 30–45 > 0–15 > 45–60 cm was observed for their respective content of total Zn as 148>126>116>114 mg/kg, while extractable Zn was observed in various depths as 0–15 > 15–30 > 30–45 > 45–60cm in the descending order of their concentration.

The content of total DTPA extractable Cd, Cu, Fe, Mn, Pb and Zn in soils irrigated with sewage by and large decreases with distance from source of sewage irrigation. Though the micronutrient was mainly restricted to 0–100m distance, the increase was appreciable in the 100–200 m range of distance from the source also. With the continuous application of sewage water for three or more years, the value of all the micronutrients shot up at the sewage source and maximum increase was for Zn followed by Cu, Mn and Fe. The increase in heavy metals was almost of the same magnitude in the distance from 0–100m and it decreased sharply afterwards. Mn and Fe appears to have migrated even beyond 200m as content was almost nearly same for Fe or may be sewage– irrigation contained negligible or very little content of Mn and Fe.

The surface soil samples from the site nearest to sewage discharge point (S_1) contained appreciably high amount of total and extractable heavy metals and gradually decreased (S_2 to S_4). The data further indicate the enrichment of extractable Cu, Pb and Zn due to discharge of sewage water in distance from the point of sewage discharge with little mobility.

From the foregoing results, it may be concluded that the concentration of Cd, Cr, Cu, Fe, Mn, Pb and Zn in the surface of soils decreased with increasing distance from sewage sludge disposal point.

Accumulation of these heavy metals was mostly confined to Plough layer, which markedly decreased upto 45 cm. depths, and there was hardly any variation in their decreasing concentrations beyond 45cm depth of the soil profile. Therefore, continuous disposal of sewage sludge to arable lands will go on increasing the concentration of these heavy metals in the feeding zone of plant roots which may not only become toxic to plants but create clinical problems in animals and human beings.

Chapter IVb

STATUS OF HEAVY METALS IN SOILS

Chapter – IVB

STATUS OF HEAVY METALS IN SOIL

Sampling sites were carefully chosen taking into consideration the ground cover, micro–relief, degree of erosion, surface drainage, proximity of trees and all other factors likely to affect the soil in comparison to the normal type. Samples were then taken as follows:

(a) Surface Soil Sampling:

After removing grasses from the surface, samples were taken from different depth from six different points in the same area using spade. All the six samples were mixed together and half a kg taken out of it, rejecting the remaining soil. Dried the sample in shade and then stored in a clean polythene bag. The polythene bag was then kept in a printed cloth bag. A proper label showing details of the sample was put inside it. A number of samples were collected in this manner. Samples were also taken from non–polluted soils. These samples were then carried to the laboratory, processed and stored for analyses.

(b) Sampling from Soil Profiles:

A few profiles were exposed with the help of spades and samples taken from different horizons. Soil samples were also collected from adjacent such fields which were not receiving sewage and industrial wastes for cultivation. These samples have been hereafter written as non–polluted. Crushed up any lumps into smaller

pieces and mixed up thoroughly on a piece of canvas. From this material taken a grab sample, i.e., spread the material into thin layer and then taken sample, small portion of the soil at random, so that each sample taken was about 1kg and was representative of the original material. The samples were placed in numbered Calico bags, giving details of location and depth of soil. Detailed notes of the samples were also taken. The samples were transported to laboratory for analyses.

Routine analysis of soil was done as per standard methods (Chopra and Kanwar, 1976 and Richards, 1954). Determination of different forms of Pb, Cu and Zn was made on clear DTPA extract, HCl extract and triacid extract usign Perkin Elmer Atomic Absorption Spectrophotometer Model 3100.

Table IVB-1: Physico–chemical properties and DTPA, 1N HCl and Tri-acid extractable forms of Cd (ppm) in polluted surface soils.

S. No.	No. of Samples	pH	$CaCO_3$	Organic Carbon %	Clay %	C.E.C.* mm/100 g soil	Cd in ppm		
							DTPA–extractable	1N HCl extractable	Triacid extractable
1.	14	7.8	2.00	0.45	23.00	13.20	1.80	1.4	4.00
2.	12	7.8	1.20	0.54	23.20	12.80	2.10	1.7	3.60
3.	10	7.6	1.00	0.58	24.70	14.20	3.50	2.8	6.00
4.	8	7.5	1.10	0.75	26.00	15.20	3.90	3.3	7.50
5.	6	7.2	0.68	0.75	25.40	15.60	5.80	5.7	7.30
6.	8	7.7	1.10	0.45	24.00	12.80	2.80	2.3	5.60
7.	10	7.8	1.20	0.45	29.90	12.60	2.30	1.9	4.10
8.	12	7.7	1.30	0.45	22.00	12.60	1.80	1.3	3.80

* C.E.C. = Cation Exchange Capacity.

Table IVB-2: Physico–chemical properties and DTPA, 1N HCl and Tri-acid extractable forms of Cr (ppm) in polluted surface soils.

S. No.	No. of Samples	pH	$CaCO_3$	Organic Carbon %	Clay %	C.E.C.* mm/100 g soil	Cr in ppm		
							DTPA–extractable	1N HCl extractable	Triacid extractable
1.	14	7.8	2.00	0.45	23.00	13.20	2.0	1.9	5.50
2.	12	7.8	1.20	0.54	23.20	12.80	3.8	3.4	8.50
3.	10	7.6	1.00	0.58	24.70	14.20	4.3	3.8	9.60
4.	8	7.5	1.10	0.75	26.00	15.20	6.7	5.7	12.90
5.	6	7.2	0.68	0.75	25.40	15.60	10.0	8.4	19.10
6.	8	7.7	1.10	0.45	24.00	12.80	2.1	2.0	4.80
7.	10	7.8	1.20	0.45	29.90	12.60	1.4	1.5	3.50
8.	12	7.7	1.30	0.45	22.00	12.60	1.1	1.1	3.00

* C.E.C. = Cation Exchange Capacity.

Table IVB-3: Physico–chemical properties and DTPA, 1N HCl and Tri-acid extractable forms of Cu (ppm) in polluted surface soils.

S. No.	No. of Samples	pH	$CaCO_3$	Organic Carbon %	Clay %	C.E.C.* mm/100 g soil	Cu in ppm		
							DTPA–extractable	1N HCl extractable	Triacid extractable
1.	14	7.8	2.00	0.45	23.00	13.20	12.42	180.46	31.80
2.	12	7.8	1.20	0.54	23.20	12.80	8.20	135.60	26.75
3.	10	7.6	1.00	0.58	24.70	14.20	18.20	240.62	41.65
4.	8	7.5	1.10	0.75	26.00	15.20	26.26	349.92	58.52
5.	6	7.2	0.68	0.75	25.40	15.60	28.20	378.20	63.73
6.	8	7.7	1.10	0.45	24.00	12.80	10.26	156.34	30.52
7.	10	7.8	1.20	0.45	29.90	12.60	8.24	136.12	26.48
8.	12	7.7	1.30	0.45	22.00	12.60	12.42	188.46	31.48

* C.E.C. = Cation Exchange Capacity.

Table IVB-4: Physico–chemical properties and DTPA, 1N HCl and Tri-acid extractable forms of Pb (ppm) in polluted surface soils.

S. No.	No. of Samples	pH	$CaCO_3$	Organic Carbon %	Clay %	C.E.C.* mm/100 g soil	Pb in ppm		
							DTPA–extractable	1N HCl extractable	Triacid extractable
1.	14	7.8	2.00	0.45	23.00	13.20	1.00	12.8	2.20
2.	12	7.8	1.20	0.54	23.20	12.80	6.60	12.5	5.40
3.	10	7.6	1.00	0.58	24.70	14.20	5.40	16.4	5.20
4.	8	7.5	1.10	0.75	26.00	15.20	7.00	20.0	5.80
5.	6	7.2	0.68	0.75	25.40	15.60	7.80	17.6	5.40
6.	8	7.7	1.10	0.45	24.00	12.80	6.10	14.5	5.20
7.	10	7.8	1.20	0.45	29.90	12.60	6.90	15.60	5.60
8.	12	7.7	1.30	0.45	22.00	12.60	1.70	8.50	1.90

* C.E.C. = Cation Exchange Capacity.

Table IVB-5: Physico–chemical properties and DTPA, 1N HCl and Tri-acid extractable from of Zn (ppm) in polluted surface soils.

S. No.	No. of Samples	pH	$CaCO_3$	Organic Carbon %	Clay %	C.E.C.* mm/100 g soil	Zn in ppm		
							DTPA–extractable	1N HCl extractable	Triacid extractable
1.	14	7.8	2.00	0.45	23.00	13.20	8.26	104.00	8.25
2.	12	7.8	1.20	0.54	23.20	12.80	8.02	104.66	8.20
3.	10	7.6	1.00	0.58	24.70	14.20	8.20	120.22	8.20
4.	8	7.5	1.10	0.75	26.00	15.20	11.24	126.26	10.12
5.	6	7.2	0.68	0.75	25.40	15.60	13.64	188.44	10.86
6.	8	7.7	1.10	0.45	24.00	12.80	8.26	84.00	8.22
7.	10	7.8	1.20	0.45	29.90	12.60	8.00	106.00	8.00
8.	12	7.7	1.30	0.45	22.00	12.60	6.86	100.00	5.68

* C.E.C. = Cation Exchange Capacity.

Table IVB-6: Distribution of DTPA Extractable Cd, Cr, Cu, Pb and Zn (ppm) in polluted soil profiles of Allahabad Region.

Site	Depth	pH	EC*	O.C.	CEC**	$CaCO_3$	Sandy Clay loam	Cd	Cr	Cu	Pb	Zn
Naini	0–18	7.6	1.58	0.72	14.88	0.78	20.0	3.75	8.52	25.26	7.6	14.64
	18–35	7.7	1.56	0.68	14.92	0.82	20.5	2.76	2.92	20.12	4.6	14.20
	35–60	7.7	1.50	0.64	15.00	1.76	21.4	1.24	1.24	15.52	1.4	2.00
	60–70	7.8	1.48	0.60	15.22	1.78	22.2	0.41	0.56	3.22	1.2	2.00
Phaphamau	0–18	7.4	1.65	0.74	14.92	0.82	19.8	3.90	8.00	23.82	7.0	13.58
	18–35	7.4	1.62	0.58	14.46	1.26	20.6	2.86	2.12	16.20	4.8	12.20
	35–60	7.7	1.59	0.38	15.52	1.96	21.2	1.02	1.80	10.52	3.1	6.00
	60–70	7.8	1.55	0.32	15.12	2.32	22.4	0.25	0.33	5.86	2.0	2.62
Jhusi	0–18	7.5	1.63	0.66	14.70	0.72	21.3	3.82	5.22	22.20	10.89	16.65
	18–35	7.7	1.61	0.56	15.28	1.24	22.4	2.42	4.42	18.32	7.5	12.68
	35–60	7.8	1.58	0.36	15.30	1.82	22.6	1.51	3.89	10.56	3.89	10.52
	60–70	8.0	1.54	0.24	15.61	1.93	23.2	0.18	1.62	4.80	2.44	5.56

Fig. IVB-1. Distribution of DTPA Extractable Cd, Pb, Cr, Cu and Zn (ppm) in polluted soil profiles of Naini.

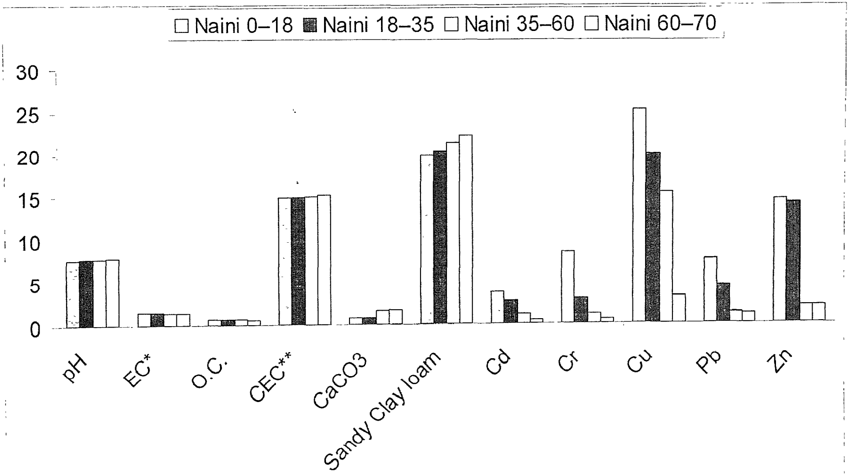


Fig. IVB-2. Distribution of DTPA Extractable Cd, Pb, Cr, Cu and Zn (ppm) in polluted soil profiles of Phaphamau.

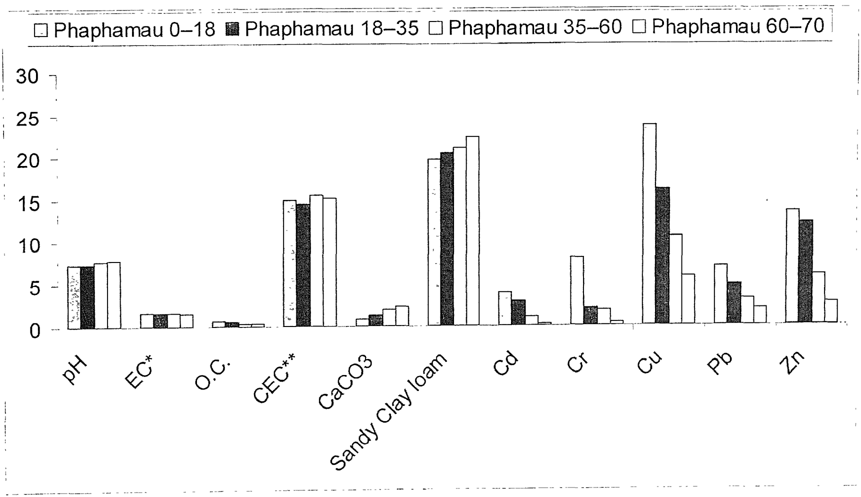


Fig. IVB-3. Distribution of DTPA Extractable Cd, Pb, Cr, Cu and Zn (ppm) in polluted soil profiles of Jhusi.

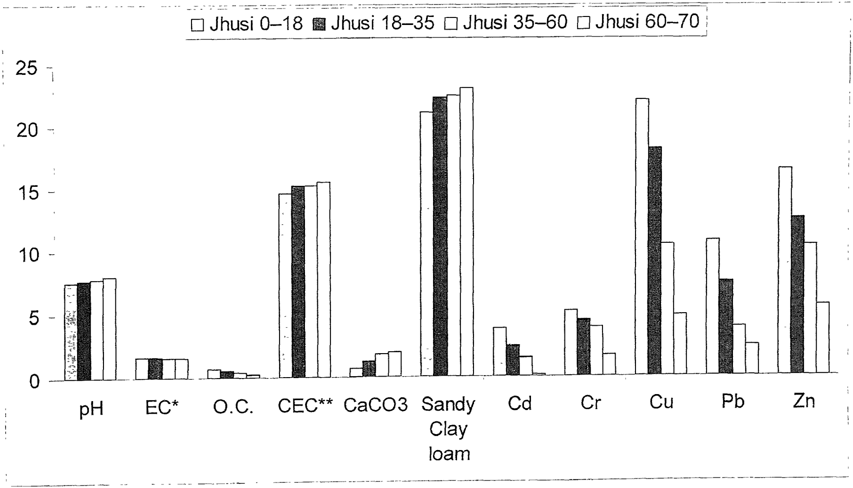


Table IVB-7: Ratio of Cd, Cr, Cu, Pb and Zn in Surface Vs. Lowermost horizon in contaminated soil profiles.

S. No.	Profile No.	Cd	Cr	Cu	Pb	Zn
1.	I	1 : 9.14	1 : 15.21	1 : 7.84	1 : 6.33	1 : 7.32
2.	II	1 : 15.6	1 : 24.14	1 : 4.06	1 : 3.5	1 : 5.18
3.	III	1 : 21.22	1 : 3.22	1 : 4.62	1 : 4.46	1 : 2.74

Table IVB-8: Distribution of DTPA extractable Cd, Pb, Cr, Cu and Zn in non–polluted (normal cultivated) soils.

I. in Surface Soils

S. No.	Soil		Properties			DTPA Extractable Metals				
	pH	$CaCO_3$	CEC	O.C.	Clay%	Cd	Cr	Cu	Pb	Zn
1.	7.2	1.54	11.0	0.24	20.0	1.5	1.4	12.2	2.0	11.2
2.	7.4	1.59	12.0	0.32	19.8	1.2	0.3	10.4	1.6	7.2
3.	7.5	1.59	12.8	0.31	19.7	0.1	0.2	8.0	0.1	5.0
4.	7.9	1.85	13.0	0.34	20.2	0.0	0.3	8.0	0.0	7.5
5.	7.6	1.61	14.3	0.32	18.8	0.1	0.6	8.0	0.0	6.4
6.	7.3	1.53	10.6	0.30	20.0	0.2	0.3	11.2	0.7	8.0
7.	7.8	1.80	11.9	0.26	20.2	0.0	0.2	6.4	0.1	7.2
8.	7.7	1.77	12.6	0.28	19.9	0.1	0.1	3.4	0.0	6.8

II. In Soils Profiles

S. No.	Depth (Cm.)	pH	$CaCO_3$	Organic Carbon %	Clay %	DTPA Extractable (ppm)				
						Cd	Cr	Cu	Pb	Zn
1.	0–18	8.2	1.52	0.33	25.0	0.2	0.1	1.15	—	1.10
2.	18–36	8.2	1.50	0.29	24.6	0.5	0.1	0.9	—	1.00
3.	35–60	8.1	1.52	0.27	24.0	0.3	0.2	1.0	—	1.07
4.	60–70	8.1	1.62	0.25	24.8	0.2	0.3	1.10	—	1.10

Table IVB-9: Correlation coefficients between Physico–chemical properties of polluted surface soils and different forms of Cd.

S. No.	Correlation between	"r"	't' test at 5% (d.f.= n–1=6)=2.447 & at 1% (d.f.=n–1=6)=3.707
1.	pH and DTPA extractable Cd	–0.964	Significant at 1%, 5%
2.	pH and HCl extractable Cd	–0.963	Significant at 1%, 5%
3.	pH and Triacid extractable Cd	–0.853	Significant at 1%, 5%
4.	$CaCO_3$ and DTPA extractable Cd	–0.754	Significant at 5%
5.	$CaCO_3$ and HCl extractable Cd	–0.734	Significant at 5%
6.	$CaCO_3$ and Triacid extractable Cd	–0.629	Non–Significant
7.	Organic carbon and DTPA extractable Cd	+0.868	Significant at 1%, 5%
8.	Organic carbon and HCl extractable Cd	+0.846	Significant at 1%, 5%
9.	Organic carbon and Triacid extractable Cd	+0.854	Significant at 1%, 5%
10.	Clay and DTPA extractable Cd	+0.830	Significant at 5%
11.	Clay and HCl extractable Cd	+0.787	Significant at 5%
12.	Clay and Triacid extractable Cd	+0.922	Significant at 1.5%
13.	C.E.C. and DTPA extractable Cd	+0.909	Significant at 1%, 5%
14.	C.E.C. and HCl extractable Cd	+0.884	Significant at 1%, 5%
15.	C.E.C. and Triacid cxtractable Cd	+0.909	Significant at 1%, 5%

Table IVB-10: Correlation coefficients between Physico–chemical properties of polluted surface soils and different forms of Cr.

S. No.	Correlation between	"r"	't' test at 5% (d.f.= n–1=6)=2.447 & at 1% (d.f.=n–1=6)=3.707
1.	pH and DTPA extractable Cr	–0.919	Significant at 1%, 5%
2.	pH and HCl extractable Cr	–0.915	Significant at 1%, 5%
3.	pH and Triacid extractable Cr	–0.902	Significant at 1%, 5%
4.	$CaCO_3$ and DTPA extractable Cr	–0.639	Non–Significant
5.	$CaCO_3$ and HCl extractable Cr	–0.642	Non–Significant
6.	$CaCO_3$ and Triacid extractable Cr	–0.609	Non–Significant
7.	Organic carbon and DTPA extractable Cr	+0.951	Significant at 1%, 5%
8.	Organic carbon and HCl extractable Cr	+0.950	Significant at 1%, 5%
9.	Organic carbon and Triacid extractable Cr	+0.942	Significant at 1%, 5%
10.	Clay and DTPA extractable Cr	+0.786	Significant at 5%
11.	Clay and HCl extractable Cr	+0.791	Significant at 5%
12.	Clay and Triacid extractable Cr	+0.771	Significant at 5%
13.	C.E.C. and DTPA extractable Cr	+0.935	Significant at 1%, 5%
14.	C.E.C. and HCl extractable Cr	+0.933	Significant at 1%, 5%
15.	C.E.C. and Triacid extractable Cr	+0.933	Significant at 1%, 5%

Table IVB-11: Correlation coefficients between Physico–chemical properties of polluted surface soils and different forms of Cu.

S. No.	Correlation between	"r"	't' test at 5% (d.f.= n–1=6)=2.447 & at 1% (d.f.=n–1=6)=3.707
1.	pH and DTPA extractable Cu	–0.855	Significant at 1%, 5%
2.	pH and HCl extractable Cu	–0.929	Significant at 1%, 5%
3.	pH and Triacid extractable Cu	–0.939	Significant at 1%, 5%
4.	$CaCO_3$ and DTPA extractable Cu	–0.395	Non–Significant
5.	$CaCO_3$ and HCl extractable Cu	–0.513	Non–Significant
6.	$CaCO_3$ and Triacid extractable Cu	–0.550	Non–Significant
7.	Organic carbon and DTPA extractable Cu	+0.852	Significant at 1%, 5%
8.	Organic carbon and HCl extractable Cu	+0.926	Significant at 1%, 5%
9.	Organic carbon and Triacid extractable Cu	+0.941	Significant at 1%, 5%
10.	Clay and DTPA extractable Cu	+0.665	Non–Significant
11.	Clay and HCl extractable Cu	+0.771	Significant at 5%
12.	Clay and Triacid extractable Cu	+0.811	Significant at 5%
13.	C.E.C. and DTPA extractable Cu	+0.809	Significant at 5%
14.	C.E.C. and HCl extractable Cu	+0.713	Significant at 5%
15.	C.E.C. and Triacid extractable Cu	+0.981	Significant at 1%, 5%

Table IVB-12: Correlation coefficients between Physico–chemical properties of polluted surface soils and different forms of Pb.

S. N.	Correlation between	"r"	't' test at 5% (d.f.= n–1=6)=2.447 & at 1% (d.f.=n–1=6)=3.707
1.	pH and DTPA extractable Pb	–0.470	Non–Significant
2.	pH and HCl extractable Pb	–0.584	Non–Significant
3.	pH and Triacid extractable Pb	–0.335	Non–Significant
4.	$CaCO_3$ and DTPA extractable Pb	–0.804	Significant at 5%
5.	$CaCO_3$ and HCl extractable Pb	–0.486	Non–Significant
6.	$CaCO_3$ and Triacid extractable Pb	–0.701	Significant 5%
7.	Organic carbon and DTPA extractable Pb	+0.588	Non–Significant
8.	Organic carbon and HCl extractable Pb	+0.755	Significant at 5%
9.	Organic carbon and Triacid extractable Pb	+0.522	Non–Significant
10.	Clay and DTPA extractable Pb	+0.736	Significant at 5%
11.	Clay and HCl extractable Pb	+0.980	Significant at 1%, 5%
12.	Clay and Triacid extractable Pb	+0.756	Significant at 5%
13.	C.E.C. and DTPA extractable Pb	+0.452	Non–Significant
14.	C.E.C. and HCl extractable Pb	+0.774	Significant at 5%
15.	C.E.C. and Triacid extractable Pb	+0.402	Non–Significant

Table IVB-13: Correlation coefficients between Physico–chemical properties of polluted surface soils and different forms of Zn.

S. N.	Correlation between	"r"	't' test at 5% (d.f.= n–1=6)=2.447 & at 1% (d.f.=n–1=6)=3.707
1.	pH and DTPA extractable Zn	–0.908	Significant at 1%, 5%
2.	pH and HCl extractable Zn	–0.910	Significant at 1%, 5%
3.	pH and Triacid extractable Zn	–0.720	Significant at 5%
4.	$CaCO_3$ and DTPA extractable Zn	–0.542	Non–Significant
5.	$CaCO_3$ and HCl extractable Zn	–0.572	Non–Significant
6.	$CaCO_3$ and Triacid extractable Zn	–0.441	Non–Significant
7.	Organic carbon and DTPA extractable Zn	+0.887	Significant at 1%, 5%
8.	Organic carbon and HCl extractable Zn	+0.815	Significant at 5%
9.	Organic carbon and Triacid extractable Zn	+0.827	Significant at 5%.
10.	Clay and DTPA extractable Zn	+0.795	Significant at 5%
11.	Clay and HCl extractable Zn	+0.613	Non–Significant
12.	Clay and Triacid extractable Zn	+0.881	Significant at 1%, 5%
13.	C.E.C. and DTPA extractable Zn	+0.904	Significant at 1%, 5%
14.	C.E.C. and HCl extractable Zn	+0.849	Significant at 1%, 5%
15.	C.E.C. and Triacid extractable Zn	+0.838	Significant at 1%, 5%

Table IVB-14: Correlation coefficients and t value between physico–chemical properties and Cd, Pb, Cr, Cu and Zn of Soil profiles of Allahabad region.

S.N.	Parameters	r value									
		Cd	t value	Pb	t value	Cr	t value	Cu	t value	Zn	t value
1.	pH	-0.832^{***}	4.754	-0.624^{**}	2.526	-0.558^{*}	2.129	-0.754^{***}	3.642	-0.622^{***}	2.518
2.	Organic carbon	-0.863^{***}	5.427	-0.647^{**}	2.684	-0.579^{**}	2.252	-0.782^{***}	3.969	-0.645^{**}	2.676
3.	C.E.C.	-0.443^{*}	1.565	-0.332^{*}	1.114	-0.297^{*}	0.986	-0.401^{*}	1.387	-0.331^{*}	1.110
4.	$CaCO_3$	-0.263^{*}	0.862	-0.197^{*}	0.635	-0.176^{*}	0.565	-0.238^{*}	0.775	-0.196^{*}	0.632
5.	Clay	-0.134^{*}	0.428	-0.100^{*}	0.318	-0.090^{*}	0.285	-0.121^{*}	0.385	-1.00^{*}	0.318

* Non–significant   ** Significant at 5%   *** Significant at both 1% & 5%

Note : Tabulated Value of t at 5% (d.f. = 10) = 2.23 and at 1% (d.f. = 10) = 3.17

The physico–chemical characterizes and distribution of different forms of Cd, Cr, Cu, Pb and Zn in polluted and non–polluted soil samples (Surface soils and soil profile) have been presented in table IVB 1 to 14 and discussed under the following heads.

STATUS OF CD IN SOIL:

(a) Distribution in Surface Soil:

The physico–chemical properties and mean contents of different forms of Cd such as DTPA, HCl and Triacid extractable are given (Table IVB 1). The data sow that the amount of Cd extracted by DTPA, 1NHCl and Triacid in ppm varied from 1.8 to 5.8, 1.3 to 5.7 and 3.8 to 7.5 respectively. The accumulation of Cd in large amounts in these soils may be attributed to continuous and massive use of chemical fertilizers specially phosphatic fertilizers which contains exceptionally large amount of Cd. Singh and Sekhon (1977) reported that different commercial fertilizers commonly use contained considerable amount of Cd. Anderson and Siman (1991) also found an increase in Cd level in soils with increaing rates of fertilizer application. The higher amount of Cd in these soils might be also due to disposal of raw sewage and industrial wastes on agricultural land of the area under study. A number of workers have also reported that continuous use of sewage sludge and industrial wastes significantly increased the heavy metal status of soils (Baerug and Martinsn 1977; Sidle and Kardos, 1977; Williams et al., 1980 and Kuhad et al. 1989a). One of the other reasons for Cd accumulation is that automobiles plying on near by

highways were contaminating the soil.

Table IV – 8 gives a picture of normal agricultural soils of area under investigation which are not under the influence of automobile exhausts and sewage and industrial wastes. DTPA extractable Cd, in surface soils varied from 0.0 to 1.5 ppm respectively.

(b) Distribution in soil profiles (Cd):

DTPA extractable Cd of soil profiles presented in Table IVB – 6 indicates their content in the surface horizons ranged from 3.75 to 3.90 ppm respectively. On the other hand, in lower most horizons Cd concentration varied from 0.18 to 0.25 ppm respectively. It is clear from the data that surface soils contain higher amount of Cd and amount decreases with the depth of soil profiles. Sewage sludge, industrial wastes, agro–chemicals and aerial contamination from automobile exhausts have possibly contributed to the high accumulation of Cd in surface soils. Comparatively less amount of Cd in deeper horizons is due to low mobility of this metals into lower horizons. Low mobility was possibly due to specific adsorption of the metals with organic matter, manganese and iron oxides.

The ratio of Cd contents in uppermost versus lowermost horizons gives the idea of level of contamination in the soils. The value greater then I indicates Cd metal contamination in the soils irrigated with discharged waters. The data given in table IVB – 7 indicate that all the three soil profiles under study were highly polluted by Cd. The extent of contamination, on the basis of this index of the three profiles under study was in the following order profile–III, profile–II, profile–I. In this way all

the three profiles under study may be considered as highly contaminated with Cd. High contamination in these profiles may be ascribed to the presence of Cd in the effluents continuously used for irrigation of the crops

In soil profiles, concentrations were 0.2 to 0.5 ppm respectively for Cd. These metals were not found below 36 cm. depth in soil profiles. Agro–chemicals including chemical fertilizers are likely to be the main reason for presence of Cd in surface soil. pH, CEC and $CaCO_3$ content of soil increased with the depth of soil profiles, whereas, organic carbon and clay content decreased. On the basis of presence of Cd in considerable amounts of even in the so called normal soils it is expected that after few years these soils are likely to be contaminated by heavy metals and will be considered as metal polluted soils, it, blind use of agro–chemicals are not checked by the formers of the area under study.

C. Interrelationship between Physico–Chemical properties of polluted soils and forms of Cd:

(i) Surface Soils

The statistical data presented in table IVB – 9 show the correlation coefficients between physico–chemical properties and DTPA, 1NHCl, Triacid extractable Cd of polluted surface soils. It is evident that Cd extracted by different extractants were significantly and negatively correlated with pH (r = –0.964, –0.963, –0.853 for DTPA, 1NHCl and Triacid extractants respectively). This indicates that pH has more significant effect on Cd. An increase in pH decreases the extractable Cd. This may be due to the precipitation of these metals at higher pH. This

finding is in accordance with the findings of santillandrano and Jurinak (1975) who reported that Cd solubility decreased in soil as pH increased. Positive correlation was also observed between Cd with C.E.C. except in case of DTPA extractable Cd where the correlation coefficient was negative. But these correlation coefficients were statistically significant.

Positive and significant correlations were found to exists between organic carbon and different forms of Cd. So, organic matter promoted the availability of these metals by supplying complexing agents that interfered with the fixation of these heavy metals. This is also because higher fraction of these metals are present in the from of organic substances which comes from sewage and industrial wastes. Baghdedy (1987) stated that higher humus content increased the heavy metal content of soils.

Similar to relation with organic carbon and Cd contents were also significantly and positively correlated with clay content. It means clay has positive influence on the extractable pool of Cd. Possibly Cd adsorbed on clay fraction. Dudås and Pawluck (1977) also observed significant positive correlation of heavy metals with silt plus clay. Perusal of the table IVB – 7 reveals that significant but negative correlations were found to exist between $CaCO_3$ and form of Cd except Triacid Cd where correlation was nonsignificant. It is possibly due to fact that lime had reduced the availability of Cd. In presence of lime in soil Cd might be precipitated as carbonates.

(ii) Soil Profile

DTPA Cd was significantly and negative correlated (Table IVB – 14) with organic carbon ($r=-0.863$) and pH ($r = 0.832$) which confirm the view

that organic matter play important role to check the mobility of Cd into lower horizons as evident from decreased organic carbon content with the depth. Non–significant but negative correlation were found to exist between DTPA Cd and other soil properties, viz, CEC (r = –0.443), $CaCO_3$ (r = –0.263) and clay (r = –0.134).

So, it is inferred that surface horizons of the soil profiles contained higher amount of Cd and decreased with the soil depth. These findings are in accordance with the findings of Chang et al. (1984), Williams et al. (1980, 1984 and 1985), they also reported that content of Cd decreased with increasing depth of soil profiles.

2. STATUS OF Cr IN SOILS:

(a) Distribution in Surface Soil:

The physico–chemical properties and means of contents of different from of Cr such as DTPA, 1N HCl and Triacid extractable are given table IVB – 2. The data show that the amount of Cr extracted by DTPA, 1N HCl and Triacid in ppm varied from 1.1 to 10.0, 1.1 to 8.4 and 3.0 to 19.1 respectively. The accumulation of Cr in large amount in these soils may be attributed to continuous and massive use of chemical fertilizers specially. The higher amount of Cr in these soils might be also due to disposal of raw sewage and industrial wastes on agricultural land of the area under study. A number of workers have also reported that continuous use of sewage sludge and industrial wastes significantly increased the heavy metal status of soils (Baerug and Martinsen, 1977; Sidle and Kardos, 1977; Williams et al. 1980

and Kuhad et al. 1989a). Content of Cr is more in soils of Naini (industrial belt). This might be due to direct content of agricultural land to industries situated in that areas. Presence of Cr in large amount in industrial wastes subsequently increased the status of Cr in these soils. Handa et al. (1983) also reported that soils of carpet industrial belt contained large amount of Cr.

The physico–chemical characteristics and distribution of Cr in non–polluted surface soils and soil profiles have be presented in table IV B – 8. It is evident that the DTPA extractable Cr in surface soils varied from 0.1 to 1.4 ppm respectively.

(b) Distribution In Soil Profiles (Cr):

DTPA extractable Cr of soil profiles presented in table IVB – 6 indicates their content in the surface horizons ranged from 5.22 to 8.52 ppm respectively. On the other hand, in lower most horizons Cr concentration varied from 0.33 to 1.62 ppm respectively. It is clear from the data that surface soils contain higher of Cr and amount decreases with the depth of soil profiles. Sewage sludge, industrial wastes, agro–chemical and aerial contamination from automobile exhausts have possibly contributed to the high accumulation of Cr in surface soils.

In soil profiles concentration were 0.1 to 0.3 ppm. pH, CEC and $CaCO_3$ content of soil increased with the depth of soil profiles, whereas, organic carbon and clay content deceased. Agro–chemicals including chemical fertilizers are likely to be the main reason for presence of Cr in surface soil. On the basis of presence of Cd, Cr, Cu, Pb and Zn in

considerable amounts of even in the so called normal soils it is expected that after few years these soils are likely to be contaminated by heavy metals and will be considered as metal polluted soils, if, blind use of agro–chemical are not checked by the formers of the area under study.

The data regarding of Cr between uppermost horizons to lowermost horizon (Table IVB – 7) clearly indicate that all the soil profile under study were highly contaminated by Cr. The extent of contamination was in the order Profile II > Profile I > Profile III. High concentration of soil by Cr was due to presence of large amount of Cr in the effluents used for irrigation of the agriculture soils of the locality along with contamination by Cr loaded particulate matter caused by automobile exhausts.

(c) Interrelationship between physico-chemical properties of polluted soil and forms of Cr:

(i) Surface Soil:

The statistical data presented in table IVB – 10 shows the correlation coefficients between physico–chemical properties and DTPA, 1N HCl and Triacid extractable Cr of polluted surface soils. It is evident that Cr extracted by different extractants were significantly and negatively correlated with pH (r = –0.919, –0.915 and –0.902). Positive correlation is also observed between Cr with CEC (r = +0.935, +0.933 and +0.933).

Positive and significant correlations were found to exist between organic carbon and different from of Cr (r = +0.951, +0.950 and +0.942). So, organic matter promoted the availability of these metals by supplying

complexing agents that interfered with the fixation of these heavy metals. This is also because higher fraction of these metals are present in the form of organic substances which comes from sewage and industrial wastes. Baghdady (1987) stated that higher humus content increased the heavy metal content of soils.

Similar to relation with organic carbon and Cr contents were also significantly and positively correlated with clay contents. It means clay has positive influences on the extractable pool of Cr. Possibly Cr adsorbed on clay fraction increased as the clay content of soil increased. Dudas and Pawluck (1977) also observed significant positive correlations of heavy metals with silt plus clay. Perusal of the table IVB – 10 reveals that non–significant and negative correlations were found to exist between $CaCO_3$ and different from of Cr (–0.639, –0.642, –0.609).

(ii) Soil Profiles:

Higher availability of Cr in surface horizons may be due to presence of the metal in the form of chelates with organic matter. This view find support from the fact that a significant negative correlation was found between organic carbon content an Cr ($r = 0.647$). Lesser amount of Cr in deeper horizons may also be due to its precipitation as insoluble hydroxides and oxides under the influence of high pH existed these. Non–significant and negative correlations were observed between DTPA extractable Cr and pH ($r = -0.558$), $CaCO_3$ ($r = -0.176$), CEC ($r = -0.297$) and clay ($r = -0.090$). Therefore, DTPA Cr is adversely affected by higher pH, CEC and clay content. (Table IVB – 14).

The correlation coefficients between physico–chemical characteristics and DTPA extractable Cr (available) in polluted soil profiles have been presented in Table IVB – 14. A cursory look of Table IVB – 14 shows that a now significant negative correlation exists between available Cr and pH, (r = –0.558), CEC (r = – 0.297), $CaCO_3$ (r = –0.176) and Clay (r = –0.090). The results clearly indicates that pH, CEC, Clay and $CaCO_3$ have adverse effect on the availability of Cr. It is possibly due to the adverse effect of pH, and $CaCO_3$ on solubility and mobility of Cr. Significant negative correlation was observed between available Cr and organic carbon (r = – 0.579).

3. STATUS OF Cu IN SOILS:

(a) Distribution in surface soils:

The physico–chemical characteristics and distribution of different forms of Cu in polluted and non–polluted soils have been presented in Table IVB – 3 and 8. It is evident from Tables that Cu extracted by DTPA, HCl and triacid in these polluted soils varied from 8.20 to 28.20 ppm, 135.60 to 378.20 ppm and 26.48 to 63.76 ppm respectively. On the other hand, for non–polluted soils, DTPA extractable Cu varied from 1.80 to 3.50 ppm, respectively. On the basis of standard proposed by Singh and Singh (1986) all the soils analysed irrespective of their source of irrigation contained large amounts of extractable Cu toxic to plants.

(b) Distribution in soil profiles:

The physico–chemical characteristics and distribution of Cu in polluted and non–polluted soil profiles have been presented in

Table IVB – 6 and 8. It is evident that the DTPA extractable Cu (available) content of these polluted soils varied from 3.22 to 25.26 ppm. In surface soils of three profiles, it ranged from 22.20 to 25.26 ppm and in deeper horizons from 3.22 to 5.86 ppm. On the other hand, for non–polluted soil profiles, it varied from 3.4 to 12.2 ppm. Evidently these soils are not deficient in available Cu, rather they are rich with respect to this heavy metal. Presence of large amounts of available Cu in these polluted soils may be due to irrigation of these soils by sewage and industrial effluents containing remarkably high concentration of Cu. Application of large amounts of agro–chemicals on these soils may also be a reason for Cu accumulation. It is evident (Table IVB – 6) that the amount of available Cu was high in surface soil layer and low in deeper layers. Singh and Singh (1986) also reported similar results in polluted soil profiles. Maximum accumulation of available Cu in upper horizon than in lower horizon is possibly due to presence of enough organic matter that interfered with Cu fixation. As a result, Cu is fixed only to a limited extent in presence of organic matter and a considerable portion of this metal remained available. Examination of Table reveals that the content of organic matter decreased with the depth of the soil profiles, resulting in decreased availability of Cu with depth. Similarly, Anderson and Nilsson (1972) reported that after 12 years of adding 84 t/ha of sludge to soil, practically most of the heavy metals including Cu remained in the surface (20 cm) soil. Table IVB – 6 also reveals that available Cu concentration in soil collected from Naini area. This is possibly due to comparatively higher concentration of Cu in the effluents of that area than Naini area.

The ratio of Cu content in uppermost versus lowermost horizons gives the idea of level of contamination in the soils. The value greater than 1 indicates Cu metal contamination in the soils irrigated with discharged waters (Kuhad et al., 1989). The data given in Table IVB – 7 indicate that all the three soil profiles under study were highly polluted by Cu. The extent of contamination, on the basis of this index of the three profiles under study was in the following order: profile–I, profile–II and profile–III. In this way all the three profiles under study may be considered as highly contaminated with Cu. High contamination in these profiles may be ascribed to the presence of Cu in the effluents continuously used for irrigation of the crops.

(c) Interrelationships between physico–chemical properties of polluted soils and forms of Cu:

(i) Surface soils:

The correlation coefficients between physico–chemical characteristics and different forms of Cu have been presented in Table IVB – 11. The result show that the amount of available Cu (DTPA extractable) increased with increase in the organic carbon in the polluted soils. DTPA extractable Cu was significantly and positively correlated with organic carbon, clay content and C.E.C., indicating association of available Cu with finer fractions of soil. Joshi et al. (1982), Singh et al. (1986) and Singh and Singh (1986) also obtained similar results. High availability of Cu in these soils was possibly due to presence of enough organic matter that had promoted the availability of Cu by supplying complexing agents that interfered with Cu fixation. There existed significant negative correlation between

available Cu and pH. Singh et al. (1986) and Singh and Singh (1986) also obtained similar results. Similar to polluted soils, non–polluted soils were not deficient in DTPA extractable Cu as they contained more than 0.6 ppm of this metal. However, consistent correlationship was not observed between available Cu and physico–chemical properties of the soils.

The results presented in Table IVB – 11 show that total Cu (HCl extractable) was also found to be positively and significantly correlated with organic carbon, and C.E.C. and negatively and significantly correlated with pH only. No significant correlation was observed between $CaCO_3$, clay content and total Cu. Similar results have been reported by Singh and Singh (1986) and Singh et al (1987). Triacid extractable Cu behaved just similar to total extractable Cu and also showed almost similar relations with physico–chemical properties of the soil.

(ii) Soil profiles:

The correlation coefficients between physico–chemical characteristics and available Cu (DTPA extractable) in polluted soil profiles have been presented in Table IVB – 14. Examination of the correlation data indicates that available Cu bears a significant negative correlation with pH and Organic Carbon. This finding is in accordance with the findings of Singh and Singh (1986) and Singh et al. (1987). It clearly indicates that pH and Organic Carbon have adverse effect on the availability of Cu. It is possibly because lime reduces the availability of Cu and high pH decreases the solubility and mobility of Cu. No significant correlation existed between available Cu and $CaCO_3$, clay content and C.E.C.

Thus, on the basis of results, it is concluded that riverside and other soils of Allahabad are highly contaminated with Cu. These contaminated soils are likely to pollute vegetable crops, animal feed and drinking and irrigation water. The soil adjacent to are comparatively more contaminated than other areas. Possible sources of Cu contamination of the soils are sewage and industrial effluents used for irrigation and fertilization of these soils. Further, surface (30cm) soils are more contaminated than deeper soil horizons, indicating low vertical mobility of Cu from upper horizon to lower horizons. Singh et al. (1987) also reported similar results.

4. STATUS OF Pb IN SOILS:

(a) Distribution in surface soils:

It is evident from Table IVB – 4 that DTPA extractable Pb (available) content varied from 1.0 to 7.8 ppm, HCl extractable Pb (total) from 8.5 to 20.0 ppm and triacid extractable Pb from 1.9 to 5.8 ppm, respectively. Similar results have been reported by Singh and Singh (1986). These soils, growing vegetable crops and receiving sewage and industrial effluents as well as large amount of fertilizers. Thus contained exceptionally higher amounts of Pb, possibly due to presence of this metal in the effluents. Intensive farming is common on these lands and large amounts of agro–chemicals are used in order to get high yield. So, large quantities of added agriculture chemicals containing Pb may also have contributed considerable amounts of this metal to the concerned soils. Presence of large amounts of Pb in these soils, which are adjacent to busy motorways, may also be due to their contamination by automobile exhausts

containing Pb. By far the major source of air borne Pb is the combustion of loaded petrol/gasoline. Pb is added in the form of tetraalkyl lead (TEL), primarily as Pb $(CH_3)_4$ and $Pb(C_2H_5)_4$ together with scavengers 1, 2–dichloroethane and 1, 2–dibromethane. Compounds (TEL) added to gasoline to reduce 'knocking' are emitted into the atmosphere with the exhausts as volatile lead halides (bromides and chlorides). In common with other particulate pollutants, Pb is removed from the atmosphere by wet and dry deposition processes. As a result, street dusts and roadside soils become enriched with Pb, with concentrations typically of the order of 1000–4000 mg kg^{-1} on busy streets.

(b) Distribution in soil profiles:

The physico–chemical characteristics and distribution of DTPA extractable Pb in polluted soil profiles have been presented in table IVB – 6.

It is evident from the table that the DTPA extractable Pb (available) content in soils under study varied from 1.2 to 10.89 ppm. In surface soils of three profiles, it ranged from 7.0 to 10.89 ppm and in deeper horizons from 1.2 to 2.44 ppm. This finding is in accordance with the findings of Singh and Singh (1986) and Singh et al. (1990). It clearly indicates that the surface soils contained higher amounts of Pb than sub–soils. Similar results have been reported by Rekha et al. (1985), Kuhad et al. (1989), Hasan (1990) and Singh et al. (1990). High concentration of Pb in these polluted soils is possibly due to the use of Pb contaminated sewage and industrial effluents applied on these soils. It is evident that the amount of available Pb

is higher in surface soil and has regularly decreased with the depth of the profiles. Pb concentration in surface layer of profiles I, II and III was 71.4, 84.2 and 89.7 percent, respectively, higher them that found at 70cm depth, indicating marked contamination of the surface soils by Pb. Continuous use of Pb–rich sewage and industrial effluents with additional aerial contamination from automobiles exhausts, has undoubtedly contributed to this high accumulation. Comparatively higher Pb concentrations.

The data regarding ratio of Pb between uppermost horizons to lowermost horizon (Table IVB – 7) clearly indicate that all the soil profile under study were highly contaminated by Pb. The extent of contamination was in the order: Profile III > Profile–I > Profile–II. High contamination of soil by Pb was due to the presence of large amount of Pb in the effluents used for irrigation of the agriculture soils of the locality along with contamination by Pb loaded particulate matter caused by automobile exhausts.

(c) Interrelationships between physico–chemical properties of polluted soils and forms of Pb:

(i) Surface Soils:

The correlation coefficient between physico–chemical properties and different forms of Pb in polluted surface soils have been presented in table (IVB – 12). It is evident from this table that available Pb shows a Non-significant, positive correlation with organic carbon but significant HCl extractable ($r = + 0.755$) and significant negative correlation with $CaCO_3$ but Non-significant HCl extractable ($r = - 0.701$). It clearly

indicates that availability of Pb increased with increase in organic carbon in the polluted soils. It was possibly due to presence of organic matter that had promoted that availability of Pb by supplying complexing agents that interfered with Pb fixation.

Correlation data also indicate that pH and $CaCO_3$ have adverse effect on the availability of Pb. High pH might have decreased the solubility and mobility of Pb. A cursory look of table indicates that IVB – 12 total Pb is Non-significantly and negatively correlated with pH and $CaCO_3$ in polluted soils. It may, therefore, be inferred that $CaCO_3$ and pH have adverse effect on the total Pb, because lime might have fixed and reduced total Pb and high pH decreased the solubility and mobility of Pb. Further existence of significant positive correlation between total Pb and organic carbon, clay content and CEC (table IVB – 12), indicate association of total Pb with finer fractions of soil. Triacid extractable Pb behaved similar of DTPA extractable Pb and also showed almost identical relations with physico–chemical properties of the soil.

(d) Soil profile:

The correlation coefficient between physico–chemical characteristics and available pH (DTPA–extractable) in polluted soil profiles have been incorporated in table IVB – 12. Examination of the correlation data indicates that Pb bears a significant negative correlation with pH and organic carbon. Therefore it may be said that pH and $CaCO_3$ have adverse effect on the availability of Pb. It is possibly because lime reduced the availability of Pb and high pH decreased the solubility and mobility of Pb.

Similar results have been reported by Singh et al. (1990). No significant correlation existed between available Pb and $CaCO_3$, clay content and C.E.C.

Correlation data also indicate in extract from soil profiles of Jhushi area (Profile–III) is possibly from surface contamination due to vehicular traffic near the sampling sites, alongwith application of such effluents on these soils, which themselves contain comparatively higher amounts of Pb. When compared with lower horizons, upper horizons had higher concentration of Pb. Bulk of the Pb remained in top (18cm.). It is interesting to note that very little movement of the metal had occurred below 40cm. Similarly Williams et al. (1980) who studied movement of metal in soil profiles, found that by application of sludge, total metal concentration increased in the surface soil. Pb moved as far into the profiles as 10cm below the mixed surface layer. Low mobility of Pb in these soils was possibly due to specific adsorption with organic matter, clay minerals, etc. Many materials present in these soils such as clays, organic acids, amino acids, humic acid, fulvic acid biological system and biological residues had possibly caused less mobility of Pb in deeper horizons. Organic compounds present in the polluted soil profiles might have formed complexes with Pb and checked its mobility in the soil. Humic and fulvic acids are considered as important organic fractions in regard to interactions with clay minerals and with metal ions in solution.

Thus, on the basis of results, it is concluded that profiles of roadside soils and other soils of Allahabad are highly contaminated by Pb. These

contaminated soils are likely to pollute vegetable crops, animal feeds and drinking and irrigation water. The soils adjacent to Jhushi area are comparatively more contaminated by Pb them other areas. Possible sources of Pb contamination of these soils are automobile exhausts and sewage effluents.

5. STATUS OF Zn IN SOILS:

(a) Distribution in surface soils:

The physico–chemical characteristics and distribution of different forms of Zn in pollute and non–polluted soils have been presented in Table IVB – 5 and 8. The results clearly indicate that DTPA extractable Zn (available) content varied from 6.86 to 13.64 ppm, HCl extractable Zn (total) from 84.0 to 188.44 ppm and triacid extractable Zn from 3.68 to 7.5 ppm in polluted surface soils. On the other hand, for non–polluted surface soils, DTPA extractable Zn varied from 5.0 to 11.2 ppm. respectively. It was observed that these soils generally contained large amounts of Zn and were not deficient in this nutrient. Polluted soils contained comparatively much more Zn than non–polluted soils. As sewage and industrial effluents contained a large amount of micronutrients including Zn, therefore, frequent irrigation with these effluents had possible increased the content of Zn in these soils. Heavy application of fertilizers and other agro–chemicals have possibly also contributed to the content of Zn. Different sources of irrigation water were also found to be contaminated with this metal and have contributed the available Zn pool of concerned soils.

(b) Distribution in soil profiles:

The physico–chemical properties and distribution of DTPA extractable Zn (available) in polluted and non–polluted soil profiles have been presented in Table IVB – 6 and 8. Examination of results revealed that the content of DTPA extractable Zn in polluted soil profiles varied from 2.0 to 16.65 ppm. In surface layer of the three profiles, it ranged from 13.58 to 16.65 ppm and in the lowermost horizon from 2.0 to 5.56 ppm. On the other hand, for non–polluted soil profiles, it varied from 1.00 to 1.10 ppm. It is, thus, evident that surface layer of the polluted soils contained relatively much higher amounts of Zn than the lower layers, Singh et al. (1988) and Kuhad et al. (1989) also reported identical results. The amounts of Zn abruptly decreased with depth, possibly due to low mobility of this metal from upper horizon to lower horizons. High organic matter in upper horizon than in lower horizons may also be reason for higher retention of Zn in upper horizon. Evidently these soils are not deficient, but sufficient in available Zn. The ratio of Zn in uppermost versus lowermost horizons has been presented in Table IVB – 7. Examination of this Table revealed that the extent of contamination of the profiles, on the basis of the ratio of uppermost to lowermost horizons, is in following descending order: profile I> profile II>profile III. So, similar to Cu, the soil profiles under study have been highly contaminated with Zn. Presence of large amounts of available Zn in these polluted soils may be due to irrigation of these soils by sewage and industrial effluents containing remarkably high concentration of Zn. Application of large amounts of agro–chemicals on these soils may also be a reason for Zn accumulation.

(c) Interrelationships between physico–chemical properties of polluted soils and forms of Zn:

(i) Surface soils:

The correlation coefficients between different forms of Zn and physico–chemical characteristics of the polluted surface soils have been presented in Table IVB – 13. The results show that there existed significant positive correlation between DTPA extractable Zn and soil organic carbon (r = +0.887), clay content (r = +0.795) and C.E.C. (r = +0.904), indicating association of these properties with available Zn. High availability of Zn in the polluted soils under study is possibly due to presence of large amounts of organic matter than had interfered the fixation of Zn in soil by forming chelates with Zn keeping a large fraction of the metal in available form. There existed significant negative correlation between available Zn and pH, that indicates adverse effect of high pH and $CaCO_3$ on the availability of Zn. Lime possibly fixed Zn in the form of calcium zincate with increase in pH. Total Zn and triacid extractable Zn also showed significant positive relationship with different soil parameters such as organic carbon, clay content and C.E.C.

From the results, it may be said that all the soils under study are not deficient in Zn, rather some of the soil samples obtained from sewage and industrial effluent treated fields may be regarded as highly contaminated with Zn.

ii) Soil profiles:

The correlation coefficients between physico-chemical characteristics and DTPA extractable Zn (available) in polluted soil profiles have been

presented in Table IVB – 14. A cursory look of Table IVB – 14 shows that a significant negative correlation exists between available Zn and organic carbon (r = –0.645). This finding is in accordance with Singh and Singh (1986). The results clearly indicate that pH and $CaCO_3$ have adverse effect on the availability of Zn. It is possibly due to the adverse effect of pH and $CaCO_3$ on solubility and mobility of Zn. $CaCO_3$ at high pH is able to fix Zn and in turn reduces its availability. No significant correlation was observed between available Zn and $CaCO_3$ clay content and C.E.C..

Chapter IVc

UPTAKE OF HEAVY METALS BY VEGETABLE CROPS

CHAPTER IV–C

UPTAKE OF HEAVY METALS BY VEGETABLE CROPS

The vast area of agriculture land of Allahabad on which vegetable crops are mainly grown in irrigated by polluted river water, sewage and Industrial effluents, which have been found to contain excessive amounts of Cd, Cr, Pb, Cu and Zn that may cause adverse effects on germination, growth and yield of food. Crops and are health hazards as many plants accumulate Cd, Cr, Pb, Cu and Zn in large amounts. Practically less information is available on the food crops grown on soils irrigated with polluted effluents. Hence, this work was planned to study:

1. The distribution of Cd, Cr, Pb and Zn in crops obtained from sewage irrigated soils in S.D.I. fields.
2. The distribution of Pb, Cu & Zn in crops obtained from roadside and other fields.

Experimental details

The nature of vegetables crops viz. spinach and fenugreek in relation to four heavy metals vis Cd, Cr, Pb and Zn was studied in a field experiment conducted at Shiela Dhar Institute experimental farm, Allahabad. The whole experiment was carried out under randomized block design.

The experimental field was nicely levelled. Composite soil samples

from 6" depth were collected by way of determining the physico–chemical properties of soil.

Treatments

1. Control (no sludge and no M.R.P.*).
2. Soil + sludge (no M.R.P.)
3. Soil + sludge + M.R.P.
4. Soil + M.R.P. (no sludge)

* M.R.P. – Mussoorie Rock Phosphate.

It was assumed that the irrigation with sewage water is not likely to affect the results because even the control plot recorded sewage irrigation.

Experiment with Spinach crop:

The experiment was conducted in 1 × 1 m^2 plots on an alluvial soil at Sheila Dhar Institute experimental farm in order to find out the affect of different doses of sludge and Mussoorie Rock Phosphate (M.R.P.) on the growth, yield and also uptake of the four pollutants viz. Cd, Cr, Pb and Zn by the vegetable crop, spinach. Dried sludge was added at the rate of 0, 12, 18, 22 t/ha. Mussoorie Rock Phosphate (containing 20.0% P_2O_5) was added at the rate of 0, 120, 140, 160 kg/ha. Thereafter, in randomized blocks 2.0 g (per plot) seeds of spinach were sown and lightly covered with the soil.

The crop was sown on 19th April, 2000. Irrigations were given at an interval of 7 to 10 days with domestic sewage water. The crop was removed along with roots after 40 days of sowing.

The total heavy metals (Cd, Cr, Pb and Zn) present in dried biomass were detected directly in tri–acid mixture extracts using Atomic Absorption Spectrophotometer.

Experiment with Fenugreek crop

The experiment was conducted in $1 \times 1\ m^2$ plots on an alluvial soil at Sheila Dhar Institute experimental farm in order to find out the effect of different doses of sludge and Mussorrie Rock Posphate (M.R.P.) on the growth, yield and uptake of four pollutants viz. Cd, Cr, Pb and Zn by a vegetable crop, Methi (Fenugreek). Dried sludge was added at the rate of 0, 8, 18, 28 t/ha and powdered Mussoorie Rock Phosphate (containing 20.0% P_2O_5) was added at the rate of 0, 110, 130, 150 kg P_2O_5/ha. Thereafter, in randomized blocks 3.0 (per plot) seeds of fenugreek were sown and lightly covered with the soil.

The crop was sown on 18th Nov. 2000. The crop was irrigated with domestic sewage water at 7 to 10 days intervals. The crop was harvested along with roots after 40 days of sowing.

The total heavy metals (Cd, Cr, Pb and Zn) present in dried biomass were detected directly in di–acid mixture extracts using Atomic Absorption Spectrophotometer.

Table IVC – 1
Average growth of spinach

S. No.	Treatment	After 15 days of sowing		After 30 days of sowing	
		Number of leaves	Height of plant (in cm.)	Number of leaves	Height of plant (in cm.)
1.	Control (sludge + M.R.P. = 0)	3	4	9	10
2.	Sludge (0) + M.R.P. (120 kg/ha)	3	5	10	11
3.	Sludge (0) + M.R.P. (140 kg/ha)	3	5	10	11
4.	Sludge (0) + M.R.P. (160 kg/ha)	4	6	10	13
5.	Sludge (12 t/ha) + M.R.P. (0)	5	6	11	13
6.	Sludge (12 t/ha) + M.R.P. (120 kg/ha)	5	7	10	14
7.	Sludge (12 t/ha) + M.R.P. (140 kg/ha)	5	6	10	13
8.	Sludge (12 t/ha) + M.R.P. (160 kg/ha)	4	6	10	13
9.	Sludge (18 t/ha) + M.R.P. (0)	4	6	11	13
10.	Sludge (18 t/ha) + M.R.P. (120 kg/ha)	4	6	10	14
11.	Sludge (18 t/ha) + M.R.P. (140 kg/ha)	5	7	11	14
12.	Sludge (18 t/ha) + M.R.P. (160 kg/ha)	4	7	11	14
13.	Sludge (22 t/ha) + M.R.P. (0)	6	9	14	15
14.	Sludge (22 t/ha) + M.R.P. (120 kg/ha)	6	16	15	16
15.	Sludge (22 t/ha) + M.R.P. (140 kg/ha)	7	11	17	19
16.	Sludge (22 t/ha) + M.R.P. (160 kg/ha)	7	11	18	21

Table IVC – 2
Average yield of Spinach

S. No.	Treatment	Green Weight gram/m^2	Dry weight gram/m^2
1.	Control (sludge + M.R.P. = 0)	250	50
2.	Sludge (0) + M.R.P. (120 kg/ha)	850	130
3.	Sludge (0) + M.R.P. (140 kg/ha)	850	130
4.	Sludge (0) + M.R.P. (160 kg/ha)	950	150
5.	Sludge (12 t/ha) + M.R.P. (0)	1150	170
6.	Sludge (12 t/ha) + M.R.P. (120 kg/ha)	1150	170
7.	Sludge (12 t/ha) + M.R.P. (140 kg/ha)	1250	170
8.	Sludge (12 t/ha) + M.R.P. (160 kg/ha)	1100	150
9.	Sludge (18 t/ha) + M.R.P. (0)	1000	150
10.	Sludge (18 t/ha) + M.R.P. (120 kg/ha)	1000	150
11.	Sludge (18 t/ha) + M.R.P. (140 kg/ha)	1400	190
12.	Sludge (18 t/ha) + M.R.P. (160 kg/ha)	1350	170
13.	Sludge (22 t/ha) + M.R.P. (0)	2000	230
14.	Sludge (22 t/ha) + M.R.P. (120 kg/ha)	2100	230
15.	Sludge (22 t/ha) + M.R.P. (140 kg/ha)	2700	250
16.	Sludge (22 t/ha) + M.R.P. (160 kg/ha)	2800	250

Fig. IVC-1. Average yield of Spinach (gm/m^2)

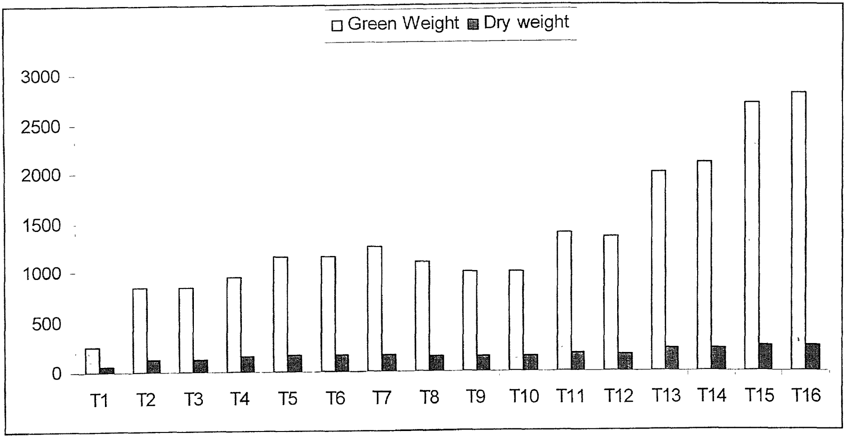


Table IVC – 3

Uptake of heavy metals by spinach–leaves

S. No.	Treatment	Heavy Metal Concentration (ppm)			
		Cd	Cr	Pb	Zn
1.	Control (sludge + M.R.P. = 0)	2.50	11.0	9.0	9.2
2.	Sludge (0) + M.R.P. (120 kg/ha)	2.20	9.9	8.6	11.2
3.	Sludge (0) + M.R.P. (140 kg/ha)	3.40	10.2	8.8	11.0
4.	Sludge (0) + M.R.P. (160 kg/ha)	3.80	10.5	8.0	10.5
5.	Sludge (12 t/ha) + M.R.P. (0)	2.15	10.4	8.4	12.9
6.	Sludge (12 t/ha) + M.R.P. (120 kg/ha)	2.20	9.5	7.5	13.2
7.	Sludge (12 t/ha) + M.R.P. (140 kg/ha)	2.30	9.8	7.8	15.2
8.	Sludge (12 t/ha) + M.R.P. (160 kg/ha)	2.10	9.9	7.5	15.6
9.	Sludge (18 t/ha) + M.R.P. (0)	2.90	9.6	8.9	16.0
10.	Sludge (18 t/ha) + M.R.P. (120 kg/ha)	2.60	10.0	8.2	13.6
11.	Sludge (18 t/ha) + M.R.P. (140 kg/ha)	3.20	9.8	7.5	14.6
12.	Sludge (18 t/ha) + M.R.P. (160 kg/ha)	2.80	9.6	7.8	16.0
13.	Sludge (22 t/ha) + M.R.P. (0)	1.90	8.9	7.2	17.0
14.	Sludge (22 t/ha) + M.R.P. (120 kg/ha)	2.10	9.8	8.5	15.4
15.	Sludge (22 t/ha) + M.R.P. (140 kg/ha)	2.00	9.2	8.2	14.9
16.	Sludge (22 t/ha) + M.R.P. (160 kg/ha)	1.80	8.5	7.0	15.2
		SE= 1.58 CD= 3.23	SE= 0.335 CD= 0.684	SE= 0.56 CD= 1.14	SE= 0.64 CD= 1.31

Fig. IVC-2. Uptake of heavy metals by spinach–leaves (ppm)

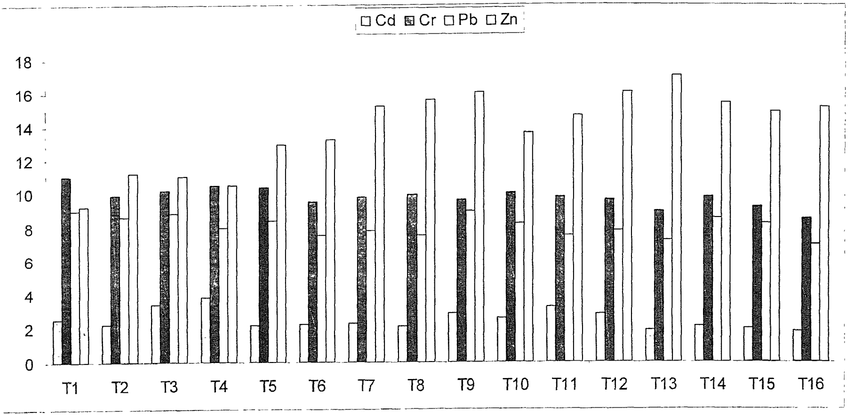


Table IVC – 4

Average growth of Fenugreek

S. No.	Treatment	After 20 days of sowing		After 40 days of sowing	
		Number of leaves	Height of plant (in cm.)	Number of leaves	Height of plant (in cm.)
1.	Control (sludge + M.R.P. = 0)	6	4	31	27
2.	Sludge (0) + M.R.P. (110 kg/ha)	7	5	33	28
3.	Sludge (0) + M.R.P. (130 kg/ha)	6	3	31	25
4.	Sludge (0) + M.R.P. (150 kg/ha)	6	3	31	25
5.	Sludge (8 t/ha) + M.R.P. (0)	6	5	33	25
6.	Sludge (8 t/ha) + M.R.P. (110 kg/ha)	6	5	35	29
7.	Sludge (8 t/ha) + M.R.P. (130 kg/ha)	5	4	31	27
8.	Sludge (8 t/ha) + M.R.P. (150 kg/ha)	4	2	27	24
9.	Sludge (18 t/ha) + M.R.P. (0)	6	4	29	25
10.	Sludge (18 t/ha) + M.R.P. (110 kg/ha)	4	3	29	25
11.	Sludge (18 t/ha) + M.R.P. (130 kg/ha)	5	3	31	27
12.	Sludge (18 t/ha) + M.R.P. (150 kg/ha)	7	4	30	27
13.	Sludge (28 t/ha) + M.R.P. (0)	6	4	34	29
14.	Sludge (28 t/ha) + M.R.P. (110 kg/ha)	6	5	31	27
15.	Sludge (28 t/ha) + M.R.P. (130 kg/ha)	6	4	35	29
16.	Sludge (28 t/ha) + M.R.P. (150 kg/ha)	6	8	40	35

Table IVC – 5
Average yield of Fenugreek

S. No.	Treatment	Green Weight gram/m^2	Dry weight gram/m^2
1.	Control (sludge + M.R.P. = 0)	250	50
2.	Sludge (0) + M.R.P. (110 kg/ha)	450	90
3.	Sludge (0) + M.R.P. (130 kg/ha)	250	50
4.	Sludge (0) + M.R.P. (150 kg/ha)	450	90
5.	Sludge (8 t/ha) + M.R.P. (0)	450	90
6.	Sludge (8 t/ha) + M.R.P. (110 kg/ha)	350	70
7.	Sludge (8 t/ha) + M.R.P. (130 kg/ha)	600	130
8.	Sludge (8 t/ha) + M.R.P. (150 kg/ha)	310	65
9.	Sludge (18 t/ha) + M.R.P. (0)	350	70
10.	Sludge (18 t/ha) + M.R.P. (110 kg/ha)	550	110
11.	Sludge (18 t/ha) + M.R.P. (130 kg/ha)	450	90
12.	Sludge (18 t/ha) + M.R.P. (150 kg/ha)	750	150
13.	Sludge (28 t/ha) + M.R.P. (0)	670	140
14.	Sludge (28 t/ha) + M.R.P. (110 kg/ha)	850	170
15.	Sludge (28 t/ha) + M.R.P. (130 kg/ha)	750	150
16.	Sludge (28 t/ha) + M.R.P. (150 kg/ha)	1250	250

Fig. IVC-3. Average yield of Fenugreek (gm/m^2)

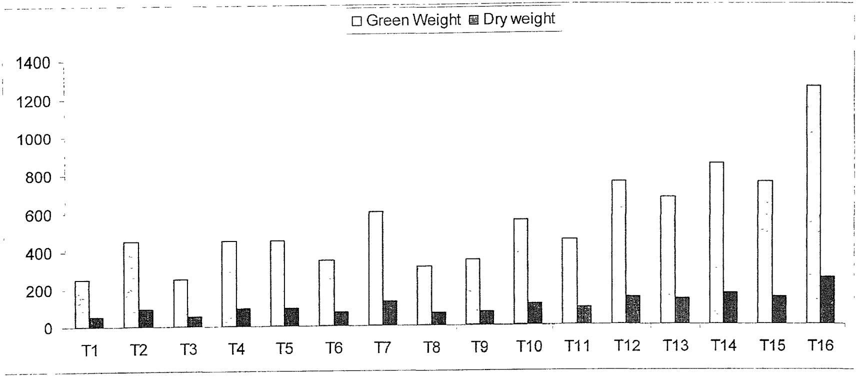


Table IVC – 6

Uptake of heavy metals by Fenugreek leaves

S. No.	Treatment	Heavy Metal Concentration (ppm)			
		Cd	Cr	Pb	Zn
1.	Control (sludge + M.R.P. = 0)	4.33	13.0	12.6	12.5
2.	Sludge (0) + M.R.P. (110 kg/ha)	3.66	13.6	12.2	15.4
3.	Sludge (0) + M.R.P. (130 kg/ha)	5.66	13.6	11.9	16.1
4.	Sludge (0) + M.R.P. (150 kg/ha)	1.33	13.0	10.0	18.3
5.	Sludge (8 t/ha) + M.R.P. (0)	4.33	12.8	12.0	16.8
6.	Sludge (8 t/ha) + M.R.P. (110 kg/ha)	7.00	11.6	12.8	19.0
7.	Sludge (8 t/ha) + M.R.P. (130 kg/ha)	6.33	11.2	12.2	20.5
8.	Sludge (8 t/ha) + M.R.P. (150 kg/ha)	5.00	10.9	11.8	20.8
9.	Sludge (18 t/ha) + M.R.P. (0)	5.66	13.7	11.6	21.6
10.	Sludge (18 t/ha) + M.R.P. (110 kg/ha)	6.33	12.2	12.0	16.5
11.	Sludge (18 t/ha) + M.R.P. (130 kg/ha)	5.00	12.5	12.2	21.9
12.	Sludge (18 t/ha) + M.R.P. (150 kg/ha)	2.33	12.4	12.2	22.3
13.	Sludge (28 t/ha) + M.R.P. (0)	1.00	11.8	11.2	19.8
14.	Sludge (28 t/ha) + M.R.P. (110 kg/ha)	5.00	10.6	10.9	20.5
15.	Sludge (28 t/ha) + M.R.P. (130 kg/ha)	3.66	12.2	10.8	22.7
16.	Sludge (28 t/ha) + M.R.P. (150 kg/ha)	3.00	11.2	11.0	20.4
		SE= 1.77 CD= 3.62	SE= 0.36 CD= 0.72	SE= 0.28 CD= 0.58	SE= 0.75 CD= 1.53

Fig. IVC-4. Uptake of heavy metals by fenugreek–leaves (ppm)

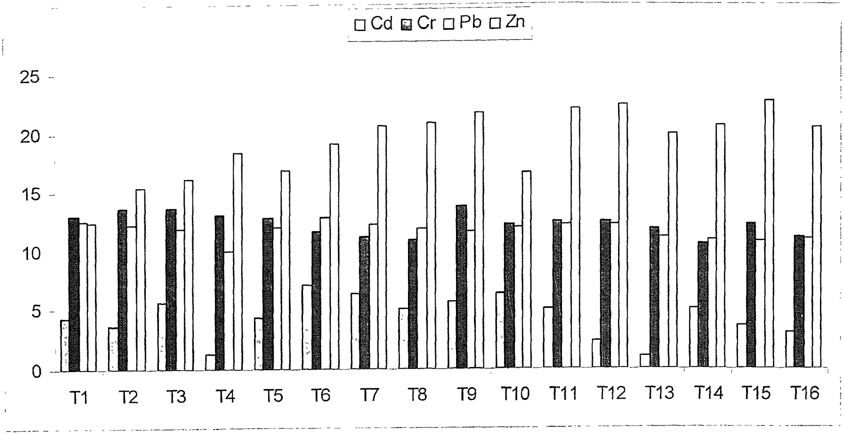


Table IVC – 7

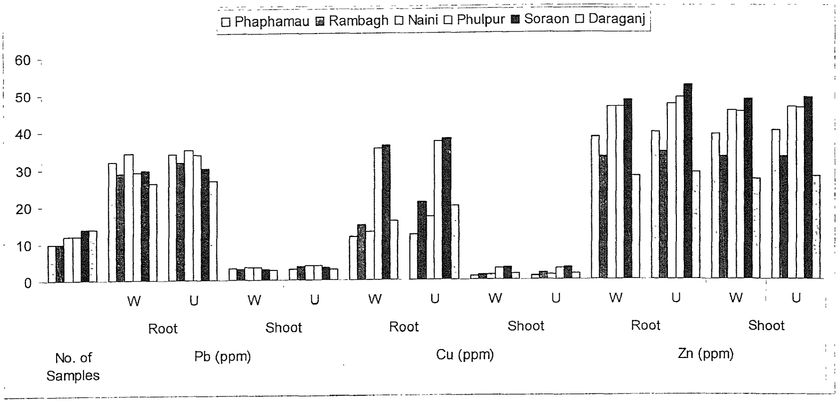
Content of Pb, Cu and Zn in radish (Raphanus safivus L.) near roadside

S. No.	Location	No. of Samples	Pb (ppm)				Cu (ppm)				Zn (ppm)			
			Root		Shoot		Root		Shoot		Root		Shoot	
			W	U	W	U	W	U	W	U	W	U	W	U
1.	Phaphamau	10	32	34.1	3.02	2.98	11.9	12.2	1.12	1.14	38.2	39.6	39.0	40.2
2.	Rambagh	10	28.8	31.6	2.92	3.55	15.0	21.0	1.44	1.73	33.1	34.2	32.9	33.0
3.	Naini	12	34.2	35.2	3.44	3.92	13.0	17.0	1.32	1.42	46.4	47.2	45.2	46.4
4.	Phulpur	12	29.2	33.8	3.35	4.00	35.4	37.2	3.13	3.14	46.3	48.9	45.1	46.0
5.	Soraon	14	29.6	30.1	2.90	3.36	36.2	38.1	3.40	3.45	48.2	52.2	48.4	48.9
6.	Daraganj	14	26.2	26.7	2.68	2.98	16.0	20.0	1.52	1.55	27.7	28.7	27.1	27.9

W = Washed

U = Unwashed

Fig. IVC-5. Content of Pb, Cu and Zn in radish (Raphanus safivus L.) near roadside (ppm)



W = Washed
U = Unwashed

Table IVC – 1, show that application of sludge @ 12, 18 and 22 t/ha remarkably increased the growth (height) of spinach plant at all stages of growth. The plot treated with M.R.P. showed leas increase in the growth of spinach in comparison to the plots receiving sludge. Maximum growth was found in plot where sludge was added @ 28 t/ha. Even 12 tones of sludge per hectare gave higher yields as compared to 120, 140 and 160 kg/ha M.R.P. Even 18 t/ha sludge and 140 t/ha M.R.P. per hectare gave higher growth as compared to 10 and 18 t/ha sludge and 120, 140 and 160 kg/ha M.R.P. Thus even a lower dost of sludge and 18 t sludge and 120 kg/ha M.R.P. Even 22 t/ha sludge and 160 kg/ha M.R.P. give higher growth as compared to all dose sludge and M.R.P. statistical analysis of the growth of spinach plant significantly increased in all the treatments over the control.

Table IVC – 4 indicates that increased doses of sludge and M.R.P. enhanced the total green biomass of fenugreek plants. Maximum biomass was found where sludge and M.R.P. was applied @ 22 t/ha and 160 kg/ha. The weight of fenugreek shoots increased with increasing of sludge and M.R.P. shoot weight of spinach was found much lower where M.R.P. was used as compared to sludge. Maximum shoot weight was found where sludge and M.R.P. was used @ 22 t/ha and 160 kg/ha. This corresponds very well with the growth of the plant. Even 22 t/ha sludge + 160 kg/h M.R.P. per hectare gave higher yields (green biomass) compared to 12, 18 and 22 t/ha sludge. Statistical analysis of the weight roots and shoots significantly increased in all plots as compared to control.

Data presented in table IVC – 3 show that the uptake of Cd, Cr, Pb and Zn by shoot increased with doses of sludge and M.R.P., however, uptake of Cd & Cr by spinach leaves was found maximum where M.R.P. was used @ 160 kg/ha. Uptake of Pb from higher level of control plots and uptake of 2n from higher level of sludge plot were used @ 22 t/ha sludge.

Table IVC – 5 show that application of sludge @ 8, 18 and 28 t/ha remarkably increased the growth (height) of fenugreek plant at all stages (20 days and 40 days of sowing) of growth. The plots treated with M.R.P. showed least increase in the growth of fenugreek in comparison to plots receiving sludge. Maximum growth was found in sludge plot where added @ 28 t/ha sludge and 150 kg/ha M.R.P. Even 28 tones of sludge per hectare gave higher yields as compared to 110, 130 & 150 kg/ha M.R.P. Even 18 t/ha sludge and 130 kg/ha M.R.P. per hectare gave higher growth as compared to 8; 18 t/ha sludge. Statistical analysis of the growth of fenugreek plant significantly increased in all the treatments over the control.

Table IVC – 6 indicates that increased doses of sludge and M.R.P. enhanced the total green biomass of fenugreek. Maximum biomass was found where sludge was applied 28 t/ha with added 150 kg/ha M.R.P. The weight of fenugreek shoot increased with increasing doses of sludge and M.R.P. shoot weight of fenugreeks was found much lower M.R.P. was used as compared to sludge. Maximum shoot weight was found where sludge and M.R.P. was applied 28 t/ha sludge and 150 kg/ha M.R.P. This

corresponds very well with the growth of the plants. Even 18 tones sludge + 130 kg M.R.P. per hectare gave higher yields (green biomass) compared to 8, 18 and 28 t/ha sludge. Statistical analysis of the results in table 27 indicates that the weight root and shoot significantly increased in all plots as compared to control.

Data presented in table IVC – 6 show that the uptake of Cd, Cr, Pb & Zn by shoot increased with increasing doses of sludge and M.R.P. However, uptake of Cd and Pb by fenugreek shoots was found maximum where sludge and M.R.P. was used 8 t sludge and 110 kg M.R.P. per hectare. Uptake of Cr from higher level of sludge plots was used @ 18 t/ha sludge and Zn from higher level of sludge (28 t/ha) and M.R.P. (130 kg/ha) plots. Statistical analysis indicates that the uptake of Cd, Cr, Pb & Zn by fenugreek shoots significantly increased in all plots as compared to control.

This is clear from the data regarding growth and yield of two crops (viz. spinach and fenugreek) that there is no harmful effect of sludge on their vegetative growth but there is a definite increase in the uptake of heavy metals by these crops when the sludge is increased.

However, when sludge is added in combination with Mussorrie Rock Phosphate, the concentration of Cd, Cr and Pb are reduced with increasing doses of Mussoorie Rock Phosphate. The content of Zn alone showed higher levels in vegetative material even in Mussoorie Rock Phosphate treated plots. The content of Zn alone showed higher levels in vegetative material even in Mussoorie Rock Phosphate treated plots. The

content of P_2O_5 in Mussoorie Rock Phosphate is about 20%.

The decrease in the uptake of pollutants like Cd, Cr and Pb after the addition of M.R.P. can be described due to antagonistic effect of phosphate on the availability of these heavy metals. Though ZnxP interaction can immobilize zinc, yet increased uptake can be explained due to higher content of zinc in the domestic sluge. Zinc is normally the most abundant heavy metal in crops, and in sewage sludges of both domestic and Industrial origin. As discussed earlier its concentration in crop is increased, sometimes substantially, as a result of addition of sludge.

In view of the harmful effects of these heavy metals, it is desirable to minimize their concentration in crops those are being grown on sludge treated land. The three interacting entities – plant, soil and sludge – may be considered in order. First, different species of plants differ greatly in their uptake of each metal, and not only do species differ but so do varieties, so that one might find a tolerant strain of a generally sensitive species. Most of the common grasses and grain crops are tolerant towards these heavy metals, while the leafy vegetables, specially the beets, are easily damaged. In our results the uptake (accumulation) of four heavy metals (Cd, Cr, Pb and Zn) by two vegetable crops followed a decreasing sequence:

Fenugreek > Spinach

Second, soils differ in two ways – firstly in colloid content and secondly in their pH. The full mechanism by which they bind heavy

metals is not well known and is controversial, but at least this is agreed. The organic colloid (humus) may be five times as effective as the same percentage of clay (the inorganic colloid). But the effect depends on pH, with a sharp increase in binding if the pH goes beyond 6. Thus acidic soils involve far more risk of damage than do those close to neutrally. The farm soil used for growing three vegetable crops had a pH 7.2 and the organic matter content was 1.2%. As the farm soil had been under sewage irrigation for a long time, the content of toxic metals is already very high.

Third, sludge itself contains high amount of Cd, Pb, Cr and Zn. The table shows the additions of these metals by the adding 8, 10 and 20 tons of sludge to the farm soil. Such an addition was purposely made in order to clarify the role of sludge in maintaining nutrient balance. The sludge inactivates the heavy metals by virtue of its own organic composition and by its content of inorganic phosphorus. The phosphate antagonizes the heavy metals inside the plant, rather than within the soil. The sludge used in experiment, contained 1.2% organic carbon and 2.0 P_2O_5 and hence the inactivation of heavy metals is most likely to occur. The heavy metals are being added through sewage irrigation as well as through sludge addition. Thus the sludge has a decisive role.

No proper information is available regarding the nature of the damage done by excess heavy metals and therefore the mechanism of resistance is not well understood.

Antagonism can play an important role in uptake of nutrients. A full mechanism of antagonism in plant physiology is beyond our scope, but it

may be of two types:

(1) Heavy metals and phosphate counteract inside the root system resulting in a mutual precipitation within the roots. This is certainly one source of damage by both Zn and Mn, but this at least should be avoided by the highly phosphate sludges or through addition of rock phosphate.

(2) The antagonism amongst heavy metals themselves which may be thought of as competition.

Additions of heavy metals to soils have usually been made in the presence of ample quantities of phosphate. Building up reserves of P is an early stage in improving agriculture, and applying the trace elements comes next. Zn deficiency in particular has occurred and continues to occur after adding ample P. Where sewage waste containing heavy metals is applied to the land, heavy amounts of P are commonly present. The question arises whether this phosphate can play a part in inactivating the excess Zn or other metals, or not? It does. There is much evidence of antagonism between individual heavy metals and phosphate but the best evidence is that the antagonism within the plant rather than in the soil. Some phosphates such as $Zn_3(PO_4)_2$ are too soluble to explain the disappearance of either Zn or P. Lead, chromium and cadmium can also interact with phosphate.

The two variables features of soil under control are organic matter content and pH. High phosphate content in sewage sludge can also help in immobilising or antagonising toxic metals. But the organic matter content

gives the greater cause for concern. Obviously there is a limit to the amount of zinc which can be inactivated by a t of organic matter. Yet once zinc is in the soil it is there for all the time, while the organic matter is open to microbial attack. Organic matter may therefore be oxidised away with increasing span of time. It can be pointed out that in spite of annual addition of sewage sludge to the Sheila Dhar Institute (SDI) experimental farm the organic carbon content has not increased beyond 1.2%.

A high initial content of the pollutants in the soil due to sewage irrigation may aggrawte the effect of adding sludge but the phosphate that is made available from the added insoluble source such as Mussoorie Rock Phosphate greatly moderated the uptake of these heavy metals.

Status of Pb, Cu and Zn in Crops Grown on road side soils:

It is evident from Table IVC – 7 that radish grown on polluted soils under investigation accumulated large amounts of Pb in their roots and shoots. The Pb content ranged from 26.2 to 34.2 ppm in washed roots and 26.7 to 35.2 ppm in unwashed roots. On the other hand, the Pb content ranged from 2.68 to 3.44 ppm in washed shoots and 2.98 to 4.00 ppm in unwashed shoots. These findings clearly indicate that unwashed roots contained slightly higher amounts of Pb than the washed roots. Similarly, unwashed shoots accumulated larger amounts of Pb than the washed shoots. Similar results have been reported by Rekha et al. (1985) and Singh (1986). Accumulation of large amounts of Pb in roots and shoots of radish in the present study was possibly due to uptake of Pb from the polluted soils in large amounts. The highest amount of Pb in samples

obtained from Naini area was possibly due to surface contamination from excessive vehicular traffic (automobiles) near sampling site in that area. The Pb may have its origin from the surface contamination due to automobile exhaust of vehicular traffic near sampling sites. These automobile exhausts containing Pb enriched dust particles ultimately fall on leaves and on soil surface, causing contamination of plant and soil. Another possible source of Pb contamination is sewage and industrial waste through irrigation and manuring resulting in increased accumulation of Pb in radish. Use of large amounts of fertilizers and manures for growing crops especially vegetables crops may also be a source of contamination. Radish grown on adjacent fields not receiving these effluents contained less amount of Pb in roots and in shoots.

Table IVC – 7 shows that the Cu content varied from 13.9 to 36.2 ppm in washed roots and 12.2 to 38.1 ppm in washed roots of radish, whereas the Cu content varied from 1.12 to 3.40 ppm in washed shoots and 1.14 to 3.45 ppm in unwashed shoots. Similarly, the Zn content varied from 27.7 to 48.9 ppm in washed roots and 28.7 to 52.2 ppm in unwashed roots of radish, whereas in shoots Zn content varied from 27.1 to 48.4 ppm in washed shoots and 27.9 to 48.9 ppm in unwashed shoots respectively. Thus, the roots contained large amount of Cu and Zn than shoots of radish. Similar results have been reported by Singh and Singh (1986) and Wallace (1989a). These findings also indicate that unwashed and the washed roots and shoots of radish are contaminated with Cu and Zn and that washing in necessary to remove these metals from roots to a larger extent. On the other hand, washing either did not remove or removed these

metals to a lesser extent from the shoots. Comparatively higher removal of these metals from roots is possibly due to washing of metal rich soil particles adhering to the roots. In other words, it can be said that in the polluted land a fraction of total Cu and Zn is present on root surface that is usually removed by washings, but washing with water is not able to remove Cu and Zn from the internal parts of the roots. Further, Cu and Zn washed from shoots is not from the surface because the quantities obtained in washed/unwashed shoots were nearly equal.

In fact, metal availability in the soil is limited by binding with humic substances as well as with clay particular and it finally depends on the CEC. Furthermore, prevention of toxic effects can be attributed to the rpesence of phosphates.

Chapter V

SUMMARY AND GENERAL DISCUSSION

Chapter – V

SUMMARY AND GENERAL DISCUSSION

In the present study toxic metals such as Cd, Cr, Pb, Cu and Zn were determined in different environmental segments such as soils, plants and water etc. Studies regarding the enrichment of heavy metals in soil profile, especially those irrigated with sewage water are lacking. The present study indicates that from the foregoing results it may be concluded that the concentration Cd, Cr, Cu, Fe, Mu and Zn in the surface of soils decreased with increasing distance from sewage sludge disposal point. Accumulation of these heavy metals was mostly confined to plough layer, which markedly decreased upto 45cm depth, and there was hardly and variation in their decreasing concentrations beyond 45cm depth of the soil profile. Therefore, continuous disposal of sewage sludge to arable lands will go on increasing the concentration of these heavy metals in the feeding zone of plant roots which may not only become toxic to plants but create clinical problems in animals and human beings.

The soil selected for study has been receiving sewage and industrial effluents as source of irrigation and manuring. The present study indicates that unfertile soils treated with sewage and industrial effluents can give better yields than the adjacent identical soils without treatment. This is probably the result of favourable pH and the greater supply of organic matter, macronutrients and trace elements. However, possibility of the increased level of heavy metals brought about by application of sewage

and industrial wastes is of great concern as it is likely to cause an elevation of Pb, Cu and Zn in crops. Similar results have been reported by Kuhad et al. (1989) and Hasan (1990). Presence of large amounts of Pb in these soils, adjacent to busy motorways, may also be due to their contamination by automobile exhausts containing Pb. The particulate matter resulting from automobile exhausts intermingled with dust continuously drops on the roadside soils under study and causes an increase in the content of Pb. Singh and Singh (1986) also reported similar results.

So far as soils of the area are concerned, they were found to contain large amount of Cd, Cr and Pb in these soils may be due to disposal of heavy metals loaded raw sewage and industrial wastes on these agricultural land. Intensive farming is also in practice especially on the land which are near to urban area. Farmers mainly use to grow vegetable crops and blindly apply fertilizers and agricultural chemicals on these lands. So, application of agricultural chemicals and fertilizers especially phosphatic fertilizers to the agricultural lands of the region is important contributors of Cd, Cr, Cu, Pb and Zn to these soils. Phosphatic fertilizers are main contributor as they contain large amounts of Cd and Pb. Mortredt et al. (1986) reported similar results. According to them, total soil Cd increased with amount of Cd applied in DAP; Cd concentration averaged 0.107 and 0.117 μg/g in soil treated with medium and high Cd DAP respectively. The Cd application rate with each of the above DAP fertilizers was 0.002, 0.036 and 0.074 Kg/ha for 2, 74 and 153 μg/g Cd containing DAP.

One of the other reasons for lead and Cadmium accumulation is that the automobiles plying on nearby highways have been enriching these soils by heavy metals every year. It is confirmed by the fact that samples taken in the beginning of research work contained less amount of the metals than those taken during last year of study. If was also observed that amount of Cd and Pb decreased as the distance from roadside increased. Major source of airborne Pb is from the combustion of petrol containing tetramethyl and tetraethyl lead, the product of combustion being particulate lead bromochloride (PbBrCl). After emission the very small particles are dispersed widely by the wind, while, coarser particles were deposited on soil and plant surface near roadside. There is evidence that lead bromochloride is converted mainly to lead sulphate and accumulated to lead oxide (PbO) or lead sulphide (PbS), and it has been suggested that these conversion occur either during transporter or after deposition on the soil. Cd resulted from attrition of Car tires and burning of diesel oil also deposited on soil surface. So, due to influences of a number of environmental pollution factors active in the region, cultivated fields have also been polluted by heavy metals similar to water resources and water–hyacinth. As soils have been polluted by Cd, Cr, Cu, Pb and Zn. Therefore, there are possibilities of concerned crops, weeds, grasses etc., growing on the soils to be polluted by Cd, Cr, Cu, Pb and Zn.

Distribution of heavy metals in soil profiles clearly indicates that surface soils contain higher amounts of Pb, Cu, Cd, Cr and Zn than lower horizons. It is interesting to note that very little movement of metal has occurred below 40cm. Williams et al. (1980) who studied movement of

metals in soil profiles also found similar results. Low mobility of Pb, Cu, Cd, Cr and Zn in the soils of Allahabad may possibly be due to specific adsorption of Pb, Cu, Cd, Cr and Zn by organic matter, clay minerals, etc. Organic compounds present in these polluted soil profiles might have formed complexes with the heavy metals and restricted their mobility in the soil.

Statistical analysis of the data has clearly indicated that physico–chemical properties of polluted soils are related with heavy metals content of the soil. Increase in content of available Pb, Cu, Cd, Cr and Zn with increase in organic matter was possibly due to supply of complexing agents by organic matter that interfere with heavy metal fixation. On the other hand, negative correlation between pH and available Pb, Cu, Cd, Cr and Zn indicate adverse effect of high pH on Pb, Cu and Zn availability possible due to decrease in the solubility and mobility of Pb, Cu, Cd, Cr and Zn at higher pH. Significant positive correlation of total soil Pb, Cu, Cd, Cr and Zn with pH and $CaCO_3$ is possibly due to decrease in solubility and mobility of these metals at high pH and fixation of these metals by $CaCO_3$. Clay fraction of the soil is also positively correlated with total Pb, Cu, Cd, Cr and Zn due to fixation of these metals by this fraction. So, roadside and other soils of Allahabad are highly contaminated with heavy metals and so also the crops, animal feeds, and water resources coming in their contact.

The ratio of metal content in uppermost versus lowermost horizons given the idea of level of contamination in the soils. The value greater

than 1 indicates metal contamination in the soil (Kuhad et al., 1989). In this way all the profiles under study may be considered as highly contaminated with Pb, Cu, Cd, Cr and Zn.

Studies with two crops (viz. spinach and fenugreek) group on S.D.I. soils reveal that there is no harmful effect of sludge on their vegetative growth but there is a definite increase in the uptake of heavy metals by these crops when the dose of sludge is increased. In view of the harmful effects of these heavy metals, it is desirable to minimize their concentration in crops those are being growth on sludge treated land. The two interacting entities–plant, soil and sludge– may be considered in order. First, different species of plants differ greatly in their uptake of each metal, and not only do species differ but so do varieties, so that one might find a tolerant strain of a generally sensitive species. Most of the common grasses and grain crops are tolerant towards these heavy metals, while the leafy vegetables, specially the beets, are easily demigod. In our results the uptake (accumulation) of four heavy metals (Cd, Cr, Pb and Zn) by Fenugreek > Spinach vegetable crops. However, when sludge is added in combination with Mussoorie Rock Phosphate, the concentration of Cd, Cr and Pb are reduced with increasing doses of Mussoori Rook Phosphate. The content of Zn alone showed higher levels in vegetative material even in M.R.P. treated plots. The decrease in the uptake of pollutants like Cd, Cr and Pb after the addition of M.R.P. can be described due to antagonistic effect of phosphate on the availability of these heavy metals. Tough Zn and P interaction can immobilize zinc, yet increased uptake can be explained due to higher content of zinc in the domestic

sludge. Zinc is normally the most abundant heavy metal in crops and in sewage sludge of both domestic and industrial origin. As discussed earlier its concentration in crops is increased, sometime substantially, as a result of additions of sludges. A high initial content of the pollutants in the soil due to sewage irrigation may aggravate the effect of adding sludge but the phosphate that is made available from the added insoluble source such as Mussoorie Rook phosphate greatly moderated the uptake of these heave metals.

Studies with crops grown on polluted soils reveal that radish (***Raphanus sativus L.***) accumulated large amounts of Pb in their roots and shoots. Unwashed roots and shoots accumulated comparatively more Pb than washed roots and shoots, possibly due to entry of Pb as fine particulate matter rich in Pb partly through stomata opening in leaves and partly through absorption by the root system. Highest amounts of Pb in samples of Naini may be due to surface contamination by excessive vehicular traffic near sampling site in that area. Williams *et al.* (1980) and Rekha *et al.* (1985) also reported almost similar results. Besides surface contamination, another possible reason is the use of heavy metal rich sewage and industrial wastes as a source of irrigation. As radish crop grown on adjacent fields, not receiving these effluents accumulated less amount of Pb. Thus, the presence of large amounts of Pb in effluents treated fields is due to presence of heavy metals in sewage and industrial effluents (Kuhad *et al.*, 1989). Similarly, it has been reported that heavy metal (mainly Cd) content of plants depends mainly on the metal concentration in the soil solution especially the divalent free heavy metal

ion (Bingham *et al.*, 1975). Crops grown on such lands also contain large amounts of Cu and Zn. Roots contain more Cu and Zn than shoots in radish. It is evident that both unwashed and washed samples of radish are contaminated with Pb, Cu and Zn, the washed samples to lesser extent than the unwashed samples. Thus, it is inferred that in these soils a fraction of total Pb, Cu and Zn is present on root surface that usually gets removed by washings. However, washing with waster is not able to remove Pb, Cu and Zn from internal part of the roots. Further, Cu and Zn in shoot washings may not be from surface contamination, because almost equal quantities were present in washed and unwashed samples. This is not true with Pb. Plant shoots are comparatively more contaminated with Pb than with Cu and Zn. This is possibly due to surface contamination of shoots by particulate matter rich in Pb. However, Cu and Zn are removed to a lesser extent than Pb by washings. This is possibly due to contamination of these crops with Pb through Pb–rich particulate matter.

Correlation studies have proved significant positive relationships between roots and shoots of radish with reference to Pb, Cu and Zn. The method are suitable for the determination of available Pb in soil. however, use of DTPA extractant should be preferred as it requires only 2 hr. for extraction in place of 16 hr as required by ammonium acetate extraction. Therefore, use of DTPA for extraction of available from of Pb may be preferred over ammonium acetate.

BIBLIOGRAPHY

BIBLIOGRAPHY

Adhikari, Subhendu, Gupta, S.K. and Banerjee, S.K. 1993. Heavy metals content of city sewage and sludge. J. Indian Sco. Soil Sci. 41 : 170–172.

Agrawal, Y.K., Patel, M.P. and Merch, S.S. 1981. Lead in soils and plants, its relationship to traffic volume and proximity to highways Lalbag, Baroda City, India. Int. J. Environ. Stud. 16 : 222–224.

Ajmal Mohammad, Ahmad Shamin and Chaudhry Rubina. 1990. Heavy metal pollution in the water and sediments of Ganga river (Narora to Kannauj). In : Intc. Conf. Heavy Metals in Indian Environment", Aligarh, India.

Albasel, N. and Cottenie, A. 1985. Heavy metal contamination near major highways, industrial and urban areas in Belgian grass land. Water, Air, Soil Pollut. 24 : 103–109.

Alegria, A., Barbera, R., Boluda, R.; Errecalde, F. and Farre, R. 1991. Environmental cadmium, lead and nickel contamination : possible relationship between soil and vegetable content. Fresenius J. Analytical Chemistry 339 : 654–657.

Andersson, A. and Siman, G. 1991. Levels of Cd and some other trace elements in soils and crops as influenced by lime and fertilizer level. Acta Agriculturae Scandinavica 41: 3–11.

Andersson, A. and Nilsson, K.O. 1972. Enrichment of trace elements from sewage sludge fertilizers in soils and plants. Ambio 1 : 176–179.

Angelidis, M. and Gibbs, R.J. 1989. Chemistry of metals in anaerobically treated sludges. Wat. Res. 23: 29–33.

Ansari, T.P.; Kazi, T.G. and Kazi, G.H. (1999). Bioavailability to vegetables of trace and toxic elements from agricultural soil and sludge amended soil. Hamdard. Medicins 42: 1, 63–67.

Baerug, R. and Martinsen, J.H. 1977. The influence of sewage sludge on the content of heavy metals in Potatoes and on tuber yield. Pl. Soil 47: 407–418.

Baghdady, N. H. 1987. Interrelationship between the soil characteristics and the total available contents of micropollutants (Cr, Ni, Cd, Pb and Hg). Mitteilungender Deustchen Bodenkundlichen Gesellschaft 55: 271–276.

Banic, S., Iretic. B., Bisic–Hajro, D. and Cordas, D. 1991. Contents of some heavy metals in the soils, plant and well water at Sarajevo airport. Radovi Polijoprivrednog Fackulteta Univerziteta U Srajevu 39: 63–72.

Basta, N. T. and Tabatabai, M.A. 1992. Effect of cropping systems on adsorption of metals by soils II. Effect of pH. Soil Sc. 153 : 195–204.

Baveye, P; McBride, M.B.; Bouldin, D; Hinesly, T.D.; Dahdoh, M.S.A. and Abdelsabour, M.F. (1999). Mass balance and distribution of sludge–borne trace elements in a silt loam soil following long–term application of sewage sludge. Science of the total environment 227: 1, 13–28.

Beckett, P.H. T. 1989. The use of extractants in studies on trace metals in soils, sewage sludges and sludge treated soils. Adv. Soil Sci., 9: 143–176.

Benedetti, A.; Figliolia, A.; Indiati, R., Izza, C. and Biondi, F.A. 1991. Effect of leather residues on the microbial turnover and plant metabolism. Chromium–phosphorus interactions. Agrochimica 35 : 111–125.

Berti, W.R. and Jacobs, L.W. (1998). Distribution of trace elements in soil from repeated sewage sludge application. Journal of Environmental Quality 27 : 6, 1280–1286.

Bingham, F.T., Page, A.L., Mahler, R.J. and Ganje, T.G. (1975) J. envir. Qual, 4, 207.

Biswa, T.D. and Mukherjee, S.K. (1990) Textbook of soil science, Tata McGraw–Hill Pub. Co. Ltd., New Delhi, P.203.

Brij Mohan, Rastogi, S.C. and Saxena, R.C. 1991. Heavy metal pollution in the aquatic environment of Kadrabad Drain Modinagar. Indian J. Environ. Prot. 11 : 216–220.

Carrao, A., Caracappa, S. and Gallo, C. 1986. Heavy metal contamination and milk composition. Atti dela Societa Italiana delle Science Veterinarie 39 : 596–599.

Cary, E.E. and Kubota, J. 1990, Chromium concentration in plants: effects of soil chromium concentration and tissue contamination by soil, J. Agric. Food Chem. 38 : 108–114.

Chandel, S.R.S. 1991. A Hand Book of Agricultural Statistics. Achal Prakashan Mandir, Kanpur, India.

Chang, A.C.; Warneke, J.E.; Page, A.L. and Lund, L.J. 1984.Accumulation of heavy metals in sewage sludge treated soils. J. Environ. Qual. 13 : 87–90.

Concentrations : VI. A model for zinc competition. Water, Air, Soil Pollut. 34 : 305–314.

Chopra, S. L. and Kanwar, J.S. 1991. Analytical Agricultural Chemistry *Kalyani Pub. New Delhi*, India.

Christensen, T.H. 1987a. Cadmium soil sorption at low concentrations: V. Evidence of competition by other heavy metals. Water, Air, Soil Pollut. 34 : 293–303.

Christensen, T.H. 1987b. Cadmium soil sorption at low concentration : VI. A model for zinc competition. Water, Air, Soil Pollut. 34: 305–314.

Colombo, L., Mangione, D.; Belhicioni, S. and Figliolia, A.; (1998). Soil profile distribution of heavy metals in a soil amended with sewage sludge for eight years. Agriculture Mediterranea, 128 : 4, 273–283.

Curzydlo, J. 1988. Content of heavy metals in soils and crop plants in the environments of the Lenin Metallurgic Works. Acta Agraria et. Silvestria 27 : 119–130.

Csillag, J.; Lukacs, A.; Bujtas, K. and Nemeth, T.; (1996). Release of Cd, Cr, Ni, Pb and Zn to the soil solution as a consequence of soil contamination and acidification. Towards sustainable land use. Furthering cooperation between people and institutions. Volume–I, No. 31, 673–680.

Dahiya, S.S.; Goel, S.; Antil, R.S. and Karwasra, S.P.S. 1987. Effect of farm yard manure and cadmium on the dry matter yield and nutrient uptake by maize. J. Indian Soc. Soil Sci. 35: 460–464.

Dani, S.P. and Dara, S.S. 1990. Studies on cadmium uptake from soils by barley plant and its effects on the chromosomes. In: Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Dang, yp; Chhabra, R; Verma, K.S. 1990. Effect of Cd, Ni, Pb and Zn on growth and chemical composition of onion and fenugreek. Communications in Soil Science And Plant Analysis, 21 : 9–10, 717–735.

Dudas, M. J. and Pawluck, S. 1977. Heavy metals in cultivated soils and cereal crops in alberta. Can. J. Soil Sci. 57 : 329–339.

El–Gende, S.A.; Abu–Sinna, SAHM and Kandil, N.F., 1999. Fractionation and accumulation of some heavy metals in soils and plants irrigated with sewage effluent. Egyptian–Journal of soil science 39: 2, 211–221.

Elsokkary, I.H. and Abdel–Salam, A.A. 1998. Bioavailability and DTPA–extractability of soil heavy metals from successive sewage sludge treated calcareous soil. Alexandria. Journal of Agricultural Research 43 : 3, 349–365 (1998).

Elkhatib, E.A.; Elshebiny, G.M. and Balba, A.M. 1991. Lead sorption in calcareous soils. Environ. Pollut. 69 : 269–276.

Eriksson, J.E. 1988. The effects of clay, organic matter and time on adsorption and plant uptake of cadmium added to the soil. Water, Air, Soil Pollut. 40 : 359–373.

Eriksson, J.E. 1989. The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to the soil. Water, Air, Soil Pollut. 48 : 317–335.

Eriksson, J.E. 1990. A field study on factors influencing Cd levels in soils and in grain of oats and winter wheat.

Fleischer, M.; Sarofim, A.F.; Fasset, D.W.; Hamond, P. Shacklette, H.T.; Nisbet, I.C.T. and Epstein, S. (1974) in Environmental Health Perspectives, May institute of Environmental Medicine, New York University Medical Center, New York, P. 253.

Fang, M. and Wong, J.W.C. 1999. Effects of lime amendment on availability of heavy metals and maturation in sewage sludge composting. Environmental Pollution 106 : 1, 83–89.

Garg, N.; Mathur, N.; Modak, D.P.; Singh, K.P.; Murthy, R.C.; Ahmed, S.; Chandra, S.V. and Ray, P.K. 1992. Trace metals trend analysis in River Ganges at Kanpur. Environ. Int. 18: 297–305.

Grun. M.; Machelett, B.; Metz, R.; Kronemann, H.; Podleask, W. and Schneider, J. 1990. Cadmium pollution of soil and plants around the sewage land application fields south of Berlin. Verband Deutscher Landwirtschaftlicher Untersuchungs and Forschungsanstalten, Reihe Kongressberichte 32: 763–768.

Gupta, V.K. and Potalia, B.S. 1990. Zinc–cadmium interaction in wheat. J. Indian Soc. Soil Sci. 38: 452–457.

Gowrek, B. 1992. Interaction of cadmium in contaminated soils using synthetic zeolites. Environ. Pollut. 75: 269–271.

Giri, A.K. and Bhattacharyya, A.K. 1999. Characterization of solid wastes generated in Wazirpur industrial area of Delhi. Journal of Ecotoxicology and Environmental Monitoring 9: 1, 51–61.

Gorlach, E. 1994. Phytoavailability of heavy metals as affected by liming and plant species. Polish Journal of soil science 27 : 1, 57–65.

Groenenberg, J.E.; Ma, W.C.; Harmscn, J.; Toosh–A–Vanden; Van–deh–Toom– A(1999). Risk analysis of fields polluted with chromium, arsenic and heavy metals at 'Zandlleij', Tilburg: ecotoxicological and soil chemical research. Ropport–DLO–Staring–Centrum–Institute No. 512. 2, 94 pp.

Haghiri, F. (1973) J. Envir., Qual. 2, 93.

Handa, B.K.; Kumar A.; Goel, D.K. and Sondhi, T.N. 1983. Pollution of ground waters by chromium in Uttar Pradesh. IAWPC Tech. Ann. X: 167–176.

Hani, H; Siegenthaler, A. and Candinas, T. 1996. Soil effects due to sewage sludge application in agriculture. Fertilizer–Research, 43: 1–3, 149–156.

Hamon, R.E.; Holm, P.E.; Lorenz, S.E.; McGrath, S.P. and Charistensenth 1999. Metal uptake by plants from sludge amended soils : caution is required in the plateau interpretation. Plant and Soil 216 : 1–2, 53–64.

Hasan, M. Z. 1990. Studies on heavy metals intake through vegetables, cereals, soils and water around an industrial city. In : Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Hickey, M.G. and Kittrick, J.A. 1984. Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. J. Environ. Qual. 13: 372–376.

Hirsch, D. and Banin. A, 1990 Cadmium speciation in soil solution. J. Environ. Qual. 19: 366–372.

Hundal, K.S. and Sandhu, S.S. 1990. Accumulation and availability of toxic metals in soils irrigated with sewage waste water. Indian J. Environ. Prot. 10: 268–273.

Ibekwe. A.M.; Angle, J.S.; Chaney, R.L.; Berkum, P, Van; Van and Berkum, P. (1995). Sewage sludge and heavy metal effects on nodulation and nitrogen fixation of legumes. Journal of Environmental–Quality 24: 6, 1199–1204.

Ihenyen, A.E. 1991. A comparative study of Pb, Cu and Cr in roadside sediments in metropolitan Lagos and Banin city, Nigeria. Environ. Int. 18 : 103–105.

Ilangovan, K. and Vivekanandan 1990. Heavy metal tolerance in rice varieties. In : Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Israili, Abdul Wahid; Nabi Ale and Naushad Ali Khan 1990. Heavy metal Pollution in ganga river at Kanpur. In : Int. 17:103–105.

Jackson, M.L. 1967. Soil Chemical Analysis. Prentice Hall of India Private Ltd. Publ., New Delhi.

Jensen, H. and Hans, M. 1990. Relative availability of 200 yr. old cadmium from soil to lettuce. Chemosphere 20 : 693–702.

Joseph, K.O., Gupta, B.P.; Muralidhar, M. and KrishNaini, K.K. 2001. Heavy metal and Pestiride studies in shrimp culture area of Nellore and Tuticorin. Proceedings of national symposium.

Joshi, H.C. 1990. Heavy metal monitoring in the hooghly estuary. In: Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Joshua, W.D.; Michalk, D.L.; Curtis, I.H.; Salt, M.; Osborne, F.G.J.; Naidu, R. 1998. The potential for contamination of soil and surface waters from sewage sludge (biosolids) in a sheep grazing study, Austrilia. Special Issues. Contaminants and the soil environment. Geoderma 84: 1–3, 135–156;

Kakati, G.N. and Bhatacharyya, K.G. 1990. Trace metals in surface water of Greater Guwahati. Indian J. Environ. Hlth. 32: 276–279.

Karagiannidis, N. 2000. Effect of Industrial Waste application on plant growth. Agro Chimica 43: 1, 18–27.

Khaled, E.M.; E.L., Sew ailem, M.S. 1999. Movement and distribution of Fe, Mn, Zn and Cu in sandy soil treated with sewage sludge. Arab Universities Journal of Agricultural–Sciences. 7:2, 615–629.

Khan, S.; Khan, N.N. and Iqbal, N. 1991. Studies on the effect of some organic pollutants on the heavy metal transport in an Indian soil. Environ. Pollut. 70 : 109–115.

King, D.L. 1988a. Retention of cadmium by several soils of the Southeastern United States. J. Environ. Qual. 17 : 246–250.

King, D.L. 1988b. Effect of selected soil properties on cadmium content of tobacco. J. Environ. Qual. 17 : 251–255.

Kirkham, M.B. (1983) Agric. Ecosystem Envir. 9, 251.

Konig, W. 1986. Heavy metal contamination of soils and crop plants subject to different pollution origins. In: Results from a survey conducted in Nordrher in–Westfalen no. 16: 239–247.

Krasniak–S.N. (1994); Mobility of heavy metals in soddy podzolic soil when applying non–conventional fertilizers. Russian–Agricultural–Sciences No.11, 37–39.

Kuhad, M.S.; Malik, R.S.; Singh, A. 1989a. Studies on mobility and accumulation of heavy metals in agricultural soil receiving sewer water irrigation. J. Indian Soc. Soil Sci. 37: 290–294.

Kuhad, M.S.; Malik, R.S.; Singh, A. and Dahiya, I.S. 1989b. Background levels of heavy metals in agricultural soils of Indo–Gangetic plains of Haryana. J. Indian Soc. Soil Sci. 37: 700–705.

Kuo, S. and Baker, A.S. 1980. Sorption of copper, zinc and cadmium by some acid soils. Soil Sci. Soc. Am. J. 44: 969–974.

Kuo, S. and McNeal, B.L. 1984. Effects of pH and phsophate on cadmium sorption by a hydrous ferric oxide. Soil Sci. Soc. Am. J. 48 : 1040–1044.

Kuo, S.; Jellum, E.J. and Baker, A.S. 1985. Effects of soil type, liming and sludge application on zinc and cadmium availability to Swisschard. Soil Sci. 139: 122–130.

Lehn, H. and Bopp, M. 1987. Prediction of heavy metal concentrations in mature plants by chemical analysis of seedlings. Pl. Soil 101: 9–14.

Li–Quoxue; Wong, J.W.C.; Wong, M.H. and Li–QX 1998. Heavy metal accumulation in chinese cabbage (Brassica chinensis) grown in soil amended with sewage sludge compost. Journal of China–Agricultural University. 3:1, 113–188.

Lund, L.J.; Page. A.L. and nelson, C.O. 1979 J. Environ. Qual. 5, 330.

Madhavi, R. and Charyulu; N.V.N. 2000. Role of certain chelates like EDTA, gypsum and serpentine soil in reducing the toxic effect of lead, cadmium and mercury on the growth and metabolism of Trigonella foenum–graecum. Plant Physiology and Biochemistry– New Delhi 25:2, 95–108.

Manko, P. and Terelak. H. 1999. Influence of sewage sludge from waste water treatment plant on the mobility of heavy metals (Zn, Cd, Pb, Cu, Ni) in the loamy soil. Folia Universitatis Agricultural Stetinesis Agriculture No. 77, 231–234.

Martinez, C.E. and Motto, H.L. 2000. Solubility of lead, Zinc and Copper added to mineral soils. Environmental – Pollution. 107: 1, 153–158.

Merry, R.H.; Tiller, K.J. and Alston, A.M. 1986. The effects of soil contamination with copper, lead and arsenic on the growth and composition of plants. Pl. Soil 95: 235–269.

Miles, L.J. and Parker, G.R. (1979), J. Envir., Qual, 8, 229.

Mira, Das; Sarkunan, V.; Misra, A.K. and Nayar, P.K. 1991. Transformation of added chromium (III) and chromium (VI) in flooded soils amended with iron, manganese and glucose. J. Environ. Sci. Health, Part A, Environ. Sci. Engineering 26: 237–247.

Misra, A.K.; Sarkunan, V.; Das, M. and Nayar, P.K. 1990. Transformation of added heavy metals in soils under flooded condition. J. Indian. Sco. Soil. Sci. 38: 416–418.

Misra, S.G. and Dinesh, Mani 1994. Uptake of heavy metals by vegetable crops grown in sewage irrigated and sludge added soils. Current–Agriculture 18: 1–2, 49–53.

Mitra, A. and Gupta, S.K. 1999. Effect of sewage water irrigation on essential plant nutrient and pollutant element status in a vegetable growing area around Calcutta. Journal of the Indian Society of Soil Science 47: 1, 99–105.

Mortvedt, J.J. 1996. Heavy metal contaminants in inorganic and organic fertilizers. Fertilizer Research, 43: 1–3, 55–61.

Moolenaar, S.W.; Beltrami, P. 1998. Heavy metal balances of an Italian soil as affected by sewage sludge and Bordeanx mixture applications. Journal of Environmental Quality, 27: 4, 828–835.

Nag, J.K. and Das, A.K. 1993. Trace metal levels in drinking water scenario of Hooghly district. Indian J. Environ. Prot. 13: 20–24.

Nand Kumar, N.V.; Khasim, D.I. and Hussain, R.C. 1990. Analysis of industrial chromium in effluent, soil and water resources and its occurrence in agricultural, animal and dairy products. In: Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Narwal, R.P.; Antil, R.S.; Gupta, A.P. 1992. Soil pollution through industrial effluent and its management. Journal of soil contamination vol.I, 1: 3, 265–272.

Nyamangara, J. and Mzezewea, J. 1999. The effect of long–term sewage sludge application on Zn, Cu, Ni and Pb levels in a clay loam soil under pasture grass in Zimbabwe. Agriculture Ecosystems and Environment. 73:3, 199–204.

Obarska–Pempkowiak, H.; Klimkowska, K.; Senesi, N. (ed) Rice, J.A. (ed.) and Miano, T.M.A. 1997. Distribution of nutrients and heavy metals in a constructed wetland system. Matter and Energy Fluxes in the Anthropocenmental Biogeochemistry, Monopoli (Bari), Itlay 21–26.

Otabbong, E. 1990. Chemistry of chromium in some Swedish soils. 6. Native P transformation and changes in pH and cation exchange capacity in two soils incubated with potassium chromate. Commun. Soil Sci. Plant Analysis 21: 687–703.

Palmer, C.D.; Wittbrodt, P.R. and Fish, W. 1990. Chromium mineral phases at a highly contaminated hard chrome plating site. Transaction of the Americal Geophysical Union 71: 1068.

Panse, V.G. and Sukhatme, P.V. 1985. Statistical Methods for Agricultural Workers. ICAR, Pub. New Delhi, India.

Pardo, R., Barrado, E.; Perez, L. and Vega, M. 1990. Determination and specification of heavy metals in sediments of the Pisuerge river. Wat. Res. 24: 373–379.

Peles, J.D.; Brewer, S.R. and Barrett, G.M. 1998. Heavy metal accumulation by old–field plant species during recovery of sludge–treated ecosystems. American–Midland Naturalist, 140: 2, 245–251.

Piper, C. S. 1950. Soil and Plant, Analysis, Univ. of Adalaid, Australia.

Podleasak, W.; Machelett, B.; Grun, M. and Garz, J. 1990. Cadmium input from mineral phsophorus fertilizers into soils of Eastern Germany, Deutscher Land wirtschaftlicher Untersuchungs and Forschungsanstalten, Relhe Kongressberichte 32: 861–866.

Pradhan, S.K.; Sarkar, S.K.; Tripathi, S.N.; Prakash, S. and Gupta, B.N. 2001. Prospects and Problems of using Domestic sewage water in Agriculture and Aquaculture. Proceedings of national symposium.

Prasad, D.D. K. and Prasad, A.R.K. 1990. Porphyrin metabolism in lead and mercury treated bajra (Pennisetum typhoideum) seedlings. J. Biosciences 15: 271–279.

Ramachandran, V. and Souza, T.J. 1998. Plant uptake of cadmium, zinc and manganese in soils amended with sewage sludge and compost. Bulletion of Environmental contamination and toxicology, 61: 3, 347–354.

Ramachandran, V.; Bhujbal, B.M. and D'Souza, T.J. 1990. Influence of rock phosphates with and without compost on the heavy metal accumulation by rice (Oryza sativa L.) grown on ultisol. In: Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Rekha, A.; Thakre, M. and Vittal Rao, M. 1985. Biomonitoring of autoexhaust pollutants with special reference to Pb. In current pollution researches in India. R.K. Trivedi and P.K. Goel (eds.). Environ. Pub., Karad, Bombay. pp 59–63.

Richards, L. A. 1954. Diagnosis and Improvement of Saline and Alkali Soils, U.S.D.A. Hand Book 60.

Rodger, G.K.; Daries, I.M. and Topping, G. 1992. Retention of trace metal contaminants in the sediment at an accumulating sewage disposal site. Wat. Res. 26 : 111–120.

Sadanandan, A.K. and Hamza, S. 2001. Studies on heavy metal residues due to continuous application of rock phosphate in sustainable Black paper production. Proceedings of national symposium.

Sakal, R.; Prasad, A.K. and Singh, A.P. 1992. Depthwise distribution of heavy metals in soils receiving sewage sludge. J. Indian Soc. Soil Sci. 40 : 732–737.

Salim A.M. 1990. Trace metal analysis of sewage sludge and soils in Bahrain. Water, Air, Soil Pollut. 51: 147–152.

Sanchez, P.G.; Fernandez, L.P.; Trejo, L.T.; Alcantar, G.G.; Cruz, J.D. and papadopoulos, A.P. 1997. Heavy metal accumulation in beans and its impact on growth and yield under soiless culture. International symposium on growing media and hydroponics Windsor, Ontario, Canada, 19–27, May. 1997.

Samaras, V.; Tsadilas–CD; Robert–PC (ed); Rust RH(ed); Larson–WE (1998). Influence of sewage sludge application on soil quality. II. Heavy metals. Proceedings of the Fourth International conference of Precision Agriculture, USA 19–22 July, 1733–1749.

Sarkunan, V., Misra, A.K. and nayar, P.K. 1989. Chromium (VI) toxicity in rice grown under flooded condition in an alluvial soil. J. Indian Soc. Soil Sci. 37: 513–517.

Sauerbeck, D.R. 1991. Plant, element and soil properties governing uptake and availability of heavy metals derived from sewage sludge. Water, Air, Soil Pollut. 57–58 : 227–237.

Sehgal, D. and Rattan, R.K. 1990. Investigations on cadmium phytotoxicity in peas on acid and alkaline soils. J. Indian Soc. Soil Sci. 38 : 561–564.

Shuvalov, Yu. N. 1989. The content of chromium in soils and its behaviour in the system soil tea plant in relation to calcium. Subtropicheskie Kut'tury 2: 32–36.

Sidle, R.C. and Kardos, L.T. 1977. Transport of heavy metals in a sludge treated forested area. J. Environ. Qual. 6 : 431–437.

Singh, A.K.; Gupta, P.L. and Singh, R.S. 1990. Levels of chromium in agricultural soils and water resources cf carpet industrial belt of Varanasi. In: Int. Symp. "New Spheres of Botanical Researches and Society", B.H.U. Varanasi, India, Dec. 26–28, p 51.

Singh, B.; Kumar, V.; Antil, R.S. and Ahlawat, V.S. 1992. Cadmium intake by wheat as influenced by nitrogen and FYM application in sandy soils. Crop Res. 5 : 243–248.

Singh, R.N. and Keffer, R.F. 1989. Uptake of nickel and cadmium by vegetables grown on soil amended with different sewage sludges. Agriculture, Ecosystem and Environment 25 : 27–38.

Singh, R.R.; Singh, V. and Shukla, A.K. 1991. Yield and heavy metal contents of berseem as influenced by sewage and refinery effluent. J. Indian Soc. Soil Sci. 39: 402–404.

Singh, R.S.; Singh, R.P.; Singh, J.; Rai, R.K. and Singh, V. B. 1992. Cd, Pb and Cr accumulation in soils and grasses under polluted environmental conditions near carpet industries. In: International Society of Soil Science Workshop, Univ. of Alberta, Canada, August, 12–15.

Singh, R.S.; Singh, R.P. and Tripathi, D.N. 1992. Utilization of pyrites for production of wheat on Cr polluted soils. Chem. Environ. Res. 1: 63–66.

Singh, R.S.; Singh, S.K.; Singh, J.; Tripathi, D.N.; Singh, R. P.; Singh, A.K. and Gupta, P.L. 1990. Distribution of DTPA extractable Pb in soil profiles contaminated to sewage and industrial effluencts. In: Int. New Sphere of Bot. Res. and Soc., B.H.U., Varanasi, Dec. 26–28.

Singh, R.S.; Singh, S.K.; Tripathi D.N. and Singh, J. 1990. DTPA extractable Pb in effluents contaminated soil profiles of Varanasi. In: Int. Conf. "Heavy Metals in Indian Environment", Aligarh, India.

Singh, R.S.; Singh, S.K.; Tripathi, D.N. and Singh, R.P. 1991. Status of Pb and Cr in water and milk samples of Varanasi, Ambe Transactions, 8: 49–57.

Singh, S.P. and Yayyar, V.K. 1991. Effect of cadmium on the growth and cadmium and zinc contents of wheat on a topic ustipsamment. J. Indian Soc. Soil Sic. 39: 204–205.

Singh, R.S. 1986. Determination of pollutants in rivers and riverside soils and crops of Varanasi. Annual Tech. Rep. CSIR (New Delhi) Project.

Singh, R.S. 1988. Determination of pollutants in rivers and riverside soil and crops of Varanasi, Inal Tech. Rep. CSIR (New Delhi) Project.

Singh, Bijay and Sekhon, G.S. 1977. Impact of fertilizers use on environmental pollution in Punjab. Present status and future projections. Fert. News 22 : 7.

Sloan, J.J.; Dowdy, R.H. and Dolan, M.S. 1998. Recovery of biosolids applied heavy metals sixteen years after application. Journal of Environmental Quality 27: 6, 1312–1317.

Soon, Y.K. and Bates, T.E. 1982. Chemical pools of cadmium, nickel and zinc in polluted soils and some preliminary indicators of their availability to plants. J. Soil Sci. 33: 477–488.

Sommers, L.E. (1997) J. Environ. Qual. 6, 225.

Srikant, R. and Reddy, S.R.P. 1991. Lead, Cadmium and Chromium levels in vegetable grown in urban sewage sludge. Food Chemistry. 40: 229–234.

Tadesse, W.; Shuford, J.W. and Taylor, R.W. 1991. Comparative availability to wheat of metals from sewage sludge and inorganic salts. Water, Air, Soil Pollut. 55: 397–408.

Totawat, K.L. 1992. Ground water pollution adjoining zinc smelters effluent stream. In: Proc. Nath. Sem. Development in Soil Science, Indian Soc. Soil Sci. pp. 154.

Tripathi, R.D.; Rai, U.N.; Sinha, S.; Garg, P. and Chandra, P. 1990. Heavy metal distribution in K.D. Pond. Unnao (U.P.) and their accumulation by aquatic plants in field and laboratory conditions. In: Int. Conf. "Heavy Metals in Indian Environemtn", Aligarh, India.

Tsadilas, C.D., Dimoyiannis, D.G.; Samaras, V. 1999; Sewage sludge usage in cotton crop. I, influence on soil properties. Pedosphere 9: 2, 147–152.

Wadge, A. and Hutton, M. 1986. The uptake of cadmium, lead and selenium by barley and cabbage grown on soils amended with refuse incinerator fly ash. Pl. Soil 96: 407–412.

Wadhawan, A.K.; Kumar Devendra, Rekha, M.P.; Chacharker and Soni, N.K. 1991. Trace and toxic metal ions in drinking water of Jodhpur. Indian J. Environ. Prot. 11: 519–524.

Wallace, A. 1989b. Plant response to some hardly known trace elements and trace element composition and distribution in plants. Soil Sci. 147: 461–464.

Warman, P.R.; Muizelaar, T. and Termeer, W.L. 1995. Bioavailability of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn from biosolids amended compost. Compost Science and Utilization 3: 4, 40–50.

Wasay, S.A.; Haw, I. and Pure, B.K. 1993. Distribution of heavy metals in a sewage oxidation pond and their adsorption in residual solid (Sewage sludge ash). Chemical–specification–and–Bioavailability. 5:4, 141–148.

Watanabe, T., Nakatsuka, H. and Ikeda, M. 1989. Cadmium and lead contents in rice available in various areas of Asia. Sci. Total Environ. 80: 175–184.

Williams. D.E., Vlamis, J., Pukite, A.H. and Corey, J.E. 1980. Trace element accumulation, movement and distribution in the soil profile from massive applications of sewage sludge. Soil Sci. 129: 119–132.

Williams, D.E. Vlamis, J.; Pukite, A.H. and Corey, J.E. 1984. Metal movement in sludge treated soils after six years of sludge addition: 1. cadmium, copper, lead and zinc. Soil Sci. 137: 351–359.

Williams, D.E.; Vlamis, J.; Pukite, A.H. and Corey, J.E. 1985. Metal movement in sludge treated soils after six years of sludge addition : 2. nickel, cobalt, iron, maganese, chromium and mercury. Soil Sci. 140: 120–125.

Witter, E. (1996). Towards zero accumulation of heavy metals in soils. An imperative or afad? Fertilizer Research 43: 1–3, 225–233.

Wong, M.H. and Chenug, Y.H. 1995. Gas production and digestion efficiency of sewage sludge containing elevated toxic metals. Bioresource–Technology. 54:3, 261–268.

Xian, X. and Shokohifard, Gholamhoss 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc and lead in polluted soils. Water, Air, Soil Pollut. 45: 265–273.

Xiong, L.M. and Lu, R.K. 1991. Influence of phosphate on transformation and plant uptake of cadmium in Cd amended soils. Pedosphere 1: 63–72.

Yamamoto, M. and Watanable, y. 1996. Behaviour of heavy metals in domestic sewage sludge amended into soils. Japanese–Journal of Science and plant Nutrition 67: 1, 24–31.

Yong, R.N.; Warkentin, B.P.; Phadungchewit, Y. and Galvez, R. 1990. Buffer capacity and lead retention in some clay materials, Water, Air, Soil Pollut. 53 : 53–67.